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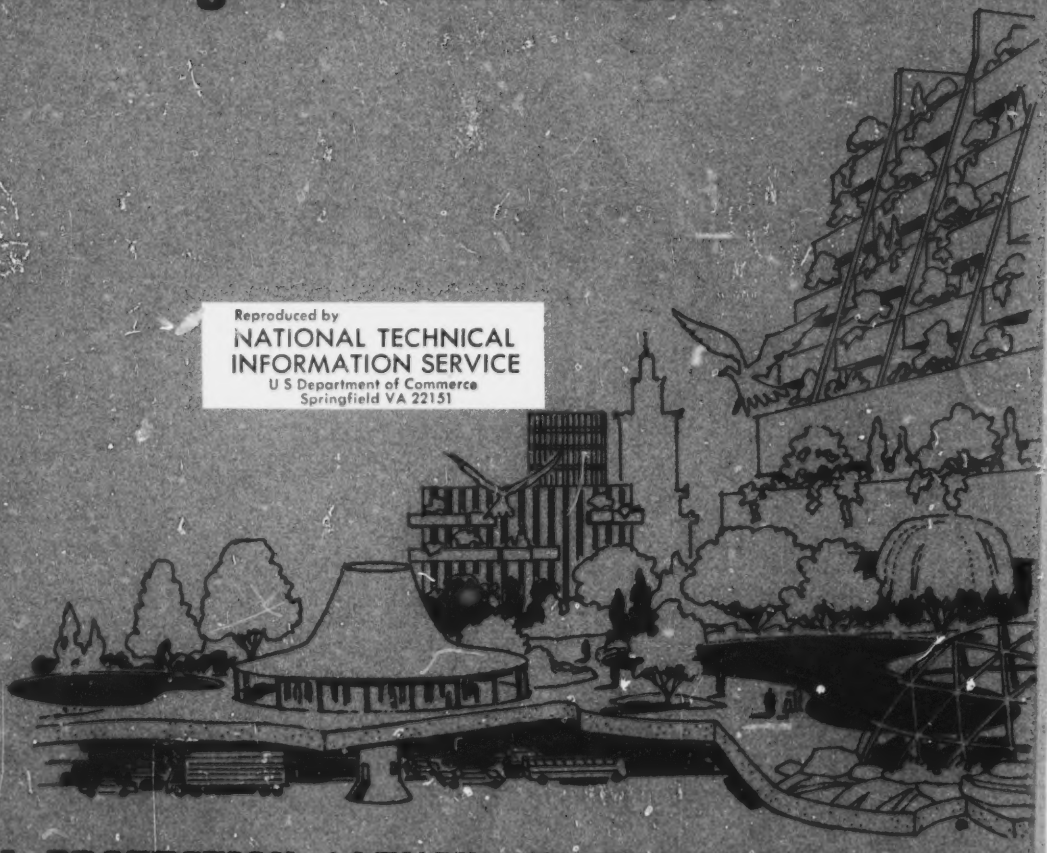

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INPUT TRANSACTION FORM

1. Report No.
2.
3. Accession No. W 72-14851

4. Title: CORROSION POTENTIAL OF NTA IN DETERGENT FORMULATIONS,

5. Report Date
6.
8. Performing Organization Report No.

7. Author(s): [redacted]

10. Project No. 16080 GPF 04/71 EPA Progress

9. Organization: Battelle Columbus Laboratories, Columbus, Ohio

11. Contract/Grant No. [redacted]

13. Type of Report and Period Covered

12. Sponsoring Organization: Environmental Protection Agency [redacted], Water Pollution Control Research Series [redacted], April 1971, 94 p., 41 fig, 28 tab, 23 ref.

16. Abstract: Coupon-weight loss and linear polarization studies were employed to investigate the corrosion potential of nitrilotriacetic acid (NTA) which is a substitute for sodium tripolyphosphate (STPP) in detergents. Solutions of 0.06, 0.12, and 0.18 weight percent using 15- and 150-ppm water hardness and temperatures of 130°F and 160°F represented laundering conditions used by the average housewife. Types 304 and 420 stainless steel and 201 Nickel were very corrosion resistant (0.01 to 0.15 mil per year), 260 Brass, electrolytic copper and 1100 Aluminum were moderately resistant (0.2 to 3 mils per year) and die-cast zinc, 1020 carbon steel and chemical lead poorly corrosion resistant at rates of 2 to 60 mils per year. NTA detergents could increase metal ion pickup at a sewage plant by a factor between 1 and 7. (Smith-Texas)

17a. Descriptors: *Corrosion, *Detergents, *Phosphates, *Nitrilotriacetic acid, Pollutants, Eutrophication, Plumbing, Stainless steel, Metals,

17b. Identifiers: *Sodium tripolyphosphate, Laundering equipment

Copy available from GPO Sup Doc [redacted], $1.00 ; microfiche from NTIS as PB 212 343, $0.95.

17c. COWRR Field & Group: 05G, 08G

18. Availability

19. Security Class. (Report)
20. Security Class. (Page)
21. No. of Pages
22. Price

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
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CORROSION POTENTIAL OF NTA IN DETERGENT FORMULATIONS

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

Project No. 16080 GPF
Contract No. 14-12-943

April, 1971

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ABSTRACT

Laboratory studies were conducted to determine the corrosion potential of nitrilotriacetic acid (NTA) as a substitute for sodium tripolyphosphate (STPP) in detergents. Coupon-weight loss and linear polarization studies were employed to investigate the corrosion of typical materials of construction which might be subject to exposure to NTA in normal use in laundering.

Detergent formulations used were representative of heavy-duty granular detergents. Solutions of 0.06, 0.12, and 0.18 weight percent using 15 and 150 ppm water hardness and temperatures of 130 and 160 F represented laundering conditions used by the average housewife.

NTA-based detergents were more corrosive by a factor between 1 and 7 to the materials: 1100 Aluminum, 260 Brass, electrolytic copper, die-cast zinc, 1020 carbon steel and chemical lead. Corrosion was generally greatest in NTA and STPP solutions with soft water. In both soft and hard waters, corrosivity increased with increase of detergent concentration.

Types 304 and 420 stainless steel and 201 Nickel were very corrosion resistant (0.01 to 0.15 mil per year), 260 Brass, electrolytic copper and 1100 Aluminum were moderately resistant (0.2 to 3 mils per year) and die-cast zinc, 1020 carbon steel and chemical lead poorly corrosion resistant at rates of 2 to 60 mils per year. Cast iron showed extreme corrosion in NTA solutions with corrosion rates between 30 and 120 mils per year. NTA detergents could increase metal ion pickup at a sewage plant by a factor between 1 and 7.

This report was submitted in fulfillment of Project Number 16080 GPF, Contract 14-12-943, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

Key Words:

corrosion, nitrilotriacetic acid (NTA), sodium tripolyphosphate (STPP), detergents, laundering materials, cast-iron sewer pipe, metal-ion pickup, pollution, coupon-weight loss, linear polarization.

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SECTION I

HISTORICAL PERSPECTIVE

This report presents the results of a research project first initiated in mid 1970. At that time, nitrilotriacetic acid (NTA) was being employed increasingly as a phosphate substitute in detergents. Due to the lack of published data on the corrosion behavior of NTA, some concern was realized for its use as a phosphate substitute in detergents. The concern led to this research project on the corrosion behavior of materials commonly used in laundering in NTA-based detergents.

The experimental work on this project began in September, 1970, prior to the statement by the Environmental Protection Agency Administrator, William D. Ruckelhaus and Surgeon General Jesse L. Steinfeld on December 18, 1970, concerning the use of NTA. In this statement, which is reproduced in full in Appendix A, the detergent manufacturers were commended for their voluntary action to discontinue the use of NTA. The discontinuation was based upon work conducted by the National Institute of Environmental Health Sciences (NIEHS). The results of this work indicated a significant increase in embryo toxicity and congenital abnormalities in rats and mice injected with dosages of two heavy metals (cadmium and methyl mercury) simultaneously with NTA compared to results with the same dosage of the metals alone. As indicated in the statement, other studies by both the industry and within the Government were underway at that time for further evaluation of NTA. The present work was allowed to continue as part of the further evaluation of this chemical.

SECTION II

CONCLUSIONS

The following major conclusions have been drawn concerning the effects of nitrilotriacetic acid (NTA)-based detergents upon materials used in laundering and in a sewer system as well as the metal-ion pickup in a sewage-treatment operation. These conclusions related to the use of detergent formulations based upon NTA and sodium tripolyphosphate (STPP) contents typical of heavy-duty granular detergents at concentrations used by the average housewife in hot water washes at 130 and 160 F with soft (15 ppm hardness) and hard (150 ppm hardness) water.

1. NTA-based detergent solutions were almost always more corrosive to the materials: 1100 Aluminum, 260 Brass, electrolytic copper, die-cast zinc, 1020 carbon steel and chemical lead than the corresponding STPP-based detergent solutions.

2. Corrosion was generally greatest in soft-water solutions and increased with increase of detergent concentration in both soft and hard water.

3. The increased corrosivity of NTA solutions over STPP solutions ranged between a factor of 1 to 7 and increased in the following order: 1100 Aluminum, chemical lead, electrolytic copper, die-cast zinc, 260 Brass, 1020 carbon steel, and uncoated cast-iron soil pipe.

4. Cast-iron soil-pipe material in the uncoated condition was not corrosion resistant to either NTA or STPP-based detergent solutions, with corrosion rates of 44 to 84 mils per year over extended periods of time. In general, the corrosion rates in the NTA solutions were higher than in corresponding STPP solutions by a factor varying between 1.6 to 6.7.

5. The materials used in laundering could be classified into the groups (a) very corrosion resistant; i.e., Types 304 and 420 stainless steel and 201 nickel (corrosion rates of 0.01 to 0.15 mil per year), (b) moderately corrosion resistant; i.e., 260 Brass, electrolytic copper and 1100 Aluminum (corrosion rates of 0.2 to 3 mils per year), (c) poor corrosion resistance; i.e., die-cast zinc, 1020 carbon steel, and chemical lead (corrosion rates of 2 to 60 mils per year) and (d) extremely poor corrosion resistance as exhibited by cast iron at rates between 16 and 120 mils per year.

6. Corrosion was usually of a general, even nature but exceptions were die-cast zinc which exhibited mostly pitting corrosion, the 1020 carbon steel which exhibited a measurable amount of localized corrosion, and brass which exhibited dezincification in some STPP-based solutions.

7. Weight-loss data were more reliable than those from the electrochemical linear polarization method with the possible exception of 1020 carbon steel, Types 304 and 420 stainless steel, and 201 Nickel. This was due to the probably related formation of films which produced a low assessment of corrosion rate by the electrochemical method.

8. Increase of detergent solution temperatures from 130 to 160 F had marginal effects on the corrosion behavior of the laundering construction materials.

SECTION III

RECOMMENDATIONS

These studies have indicated that NTA-based detergent formulations are more corrosive to most common laundering materials than the corresponding STPP-based detergent formulations. Therefore, caution should be exercised in the choice of materials with which they are to be used. It should be recognized that the NTA formulations in the absence of corrosion inhibitors, could give rise to as much as 7 times more metal-ion pick up in a sewage plant operation than for corresponding STPP formulations and thus methods for additional metal-ion removal need to be considered.

Due to the recent voluntary removal of NTA from detergent formulations, the current interest in these detergent formulations as possible aggressive corrodents has decreased. However, a variety of detergent formulations based upon soda ash, silicates, borax, polyelectrolytes, or mixtures with other minor ingredients are now available as "phosphate free" and "NTA free" detergents. These formulations needed to be studied with regard to corrosion behavior of laundering materials in the same manner as for NTA. After discussion with detergent manufacturers, it is also apparent that porcelain ceramic should be added to the list of laundering materials since it is commonly employed and is not inert to corrosion in detergent solutions as might be anticipated.

SECTION IV

INTRODUCTION

The world-wide production of detergents and cleaning agents reached an estimated 9.7 million metric tons (21,340 pounds) in 1969, up 8 percent from 1968[1]. About 25 percent or 2.4 million metric tons (5,280 pounds) was produced in the USA. Detergents and cleaning agents may contain(*) between 1 and 74 weight percent phosphates as sodium tripolyphosphate (STPP).[2] Since it has been feared that phosphates contribute to eutrophication of the Nation's lakes and streams, concern has arisen over the presence of phosphates in these products. Although it is asserted that many other materials can stimulate eutrophication, detergent producers have searched for a substitute for STPP in detergents and cleaning agents. As indicated by a state-of-the-art report (Appendix B), a substitute to replace all STPP's attributes as a detergent 'builder' has been difficult to find but some success was achieved with sodium nitrilotriacetic acid (NTA) as a partial replacement. Detergents, therefore, became available to the housewife which contained partial replacement of the STPP content with NTA. As much as 25 percent replacement of the STPP content with NTA was reported for some products.

A complete lack of corrosion data in the open literature as evidenced by a state-of-the-art report (Appendix B) indicated a need for an understanding of the corrosion behavior of NTA-based detergents. The corrosion behavior of these detergents was particularly required with respect to their effect upon

(1) Materials of construction employed in laundering
(2) Materials of construction of a sewer system
(3) The metal-ion pickup in a sewage treatment operation.

This report describes the results of experimental work conducted to determine these effects.

(*) Effective February 1, 1971, Chicago has regulated all laundry detergents to not contain more than 8.7 percent phosphorous (about 34 weight percent STPP). The House Government Operations Committee's panel on resources has recommended that phosphate be removed from detergents by 1972.

SECTION V

DISCUSSION OF THE PROBLEM

Hard waters are generally less corrosive to metals than soft waters since deposited mineral scales from hard waters retard the corrosion processes. The addition of a detergent to the water makes it less hard and, therefore, generally more corrosive. In typical detergents, the STPP or NTA builders sequester the calcium and magnesium ions and render the water less hard. The sequestering power of the builders can also lead to attack of scale on metals thay may have already been present and thus present the opportunity for corrosion. The sequestration of metal ions by STPP or NTA disturbs the metal/metal ion equilibrium and leads to increased metal dissolution. On the other hand, phosphates can promote phosphate films on some metal surfaces which can provide some protection. As described later (Appendix B), the greater sequestering ability of NTA over STPP coupled with a greater buffering capacity indicated a need for some concern of the corrosion behavior of NTA-based detergents toward metals.

The concern for corrosion of materials used in laundering indicated a need for the study of the following metals:

1100 Aluminum
260 (or 70/30) Brass
electrolytic copper
die-cast zinc
201 Nickel
Type 304 stainless steel
Type 420 stainless steel
1020 carbon steel
chemical lead

In addition to the above metals, there was a need to study the corrosion behavior of cast-iron soil pipe employed in sewer systems.

Discussions were conducted with representatives of a leading detergent producer to determine detergent formulations, detergent solution concentrations, and temperatures most representative of laundering conditions. The following facts were obtained and utilized in establishing the experimental program.

1. As there is an insufficient difference in the chemical makeup of hot and cold water-type detergents, linear alkyl sulfonate (LAS)-based granular detergents suffice for evaluation purposes.

It was believed, therefore, that corrosion studies needed to be conducted in a typical LAS-based granular detergent formulation such as:

50 weight percent STPP
20 weight percent LAS
18 weight percent fillers
6 weight percent sodium silicate
(1.6:1 SiO_2 to Na_2O ratio)
6 weight percent water

in which (a) no STPP was replaced, (b) all STPP was replaced with NTA, and (c) 25 percent of the STPP was replaced by NTA. It was intended that such formulations would not include the presence of corrosion inhibitors, fluorescents, antitarnishing agents, brighteners, etc., since such additions would not relate to all types of detergents.

2. One cup (76g) of detergent powder per 17-gallon washing machine, which corresponds to a 0.12 weight percent detergent concentration, is normally employed by the housewife.

It appeared, therefore, that solution concentrations of 0.06, 0.12, and 0.18 weight percent were required to be studied as related to under average, average, and above average detergent strengths.

3. The average hot-water wash is about 130 F but a minority employ 160 F. Solutions entering the drain are normally about 115 to 120 F.

These figures indicated that the majority of studies should be conducted at 130 F but that some evaluations should also be made at 160 F. The temperature of 130 F also appeared applicable for studies relating to temporary conditions in a sewer system drain pipe.

4. The hardness of the water is critical. It was believed, therefore, that hard and soft water conditions needed to be evaluated and that 150 ppm and 15 ppm of simulated water hardness would typify these conditions respectively.

In summary, therefore, a research program was established to employ a 50-weight percent STPP-based detergent with (a) no STPP replacement, (b) all STPP replaced by NTA, and (c) 25 percent of STPP replaced by NTA at three detergent concentrations of 0.06, 0.12, and 0.18 weight percent using waters of 15 and 150 ppm hardness and temperatures of 130 and 160 F.

Coupon weight-loss data was considered the most reliable method of corrosion evaluation of the metals since electrochemical data in such environments is very limited. Coupon weight-loss data was, therefore, used as the major evaluation method. However, it was considered that limited electrochemical "linear polarization" studies could possibly aid evaluation due to its faster measuring ability and more sensitivity to low corrosion rates.

SECTION VI

MATERIALS

Metals

All metals employed in the corrosion research program were obtained from commercial vendors. Thus, the metals were representative of materials employed commercially in everyday use. The nominal chemical composition of the metals are given in Table 1. The cast-iron material was obtained from an unused section of common soil pipe employed in a sewer system; the determined chemical composition of the cast iron is also included in Table 1.

Table 1. Nominal Composition of Metals

Metal	Composition, weight percent[a]
1100 Aluminum	99.00 Al min., 1.0 Fe plus Si max, 0.20 Cu max, 0.05 Mn max, 0.10 Zn max
1020 Carbon Steel	0.18-0.23 C, 0.30-0.60 Mn, 0.040 P max, 0.050 S max, remainder Fe
Type 304 Stainless Steel	0.08 C min, 1.0 Mn max, 1.0 Si max, 18.0-20.0 Cr, 8.0-12.0 Ni, remainder Fe
Type 420 Stainless Steel	0.15 C min, 1.0 Mn max, 1.0 Si max, 12.0-14.0 Cr, remainder Fe
201 Nickel[b]	99.5 Ni, 0.01 C, 0.20 Mn, 0.15 Fe, 0.05 Si, 0.05 Cu, 0.005 S
Electrolytic Copper	99.95 Cu, 0.04 O
260 Brass[c]	68.5-71.5 Cu, 0.07 Pb max, 0.05 Fe max, remainder Zn
Die-Cast Zinc	0.25 Cu max, 3.5-4.3 Al, 0.03-0.08 Mg, 0.007 Pb max, 0.005 Cd max, 0.005 Sn max, remainder Zn
Chemical Lead	99.90 Pb min
Cast Iron	3.50 C, 2.02 Si, 0.42 P, 0.38 Mn, 0.13 S, remainder Fe

(a) Metals Handbook, Volume 1, Properties and Selection, ASM, Ohio (1961).
(b) INCO Nickel Number 201.
(c) Copper Alloy Number 260, also termed 70/30 Brass or Cartridge Brass.

Detergent Ingredients

Basic chemical ingredients, as used in the preparation of typical heavy-duty type granular detergents, were obtained from a leading detergent manufacturer.

A linear alkyl sulfonate (LAS) solution containing 27.4 weight percent LAS, 24.1 weight percent fillers and 48.5 weight percent water together with a sodium silicate solution containing 43 weight percent sodium silicate (SiO_2 : Na_2O weight ratio of 1.6) and 57 weight percent water were used as a base in all detergent formulations.

Sodium tripolyphosphate (STPP) as obtained from the detergent manufacturer was found to be 93.3 percent pure based upon its sodium ion content for the salt $Na_5P_3O_{10}$. Impurities were identified at the following levels (as parts per million by weight):

	Cl	K	Be	Mg	Ca	Fe	Si
(ppm)	820	500	10	5	2	1	1

Sodium nitrilotriacetic acid (NTA) as obtained from government sources was a mixture of commercial products. The mixture was found to be 100 percent based upon carbon, nitrogen, and the salt $C_6H_8O_7NNa_3$; i.e., the trisodium monohydrate salt $N(CH_2COONa)_3 \cdot 1H_2O$. The sodium ion content indicated the presence of a small amount of free alkali in the salt. Impurities were identified at the following levels (as parts per million by weight):

	Cl	K	B	Fe	Mg	Ca	Si
(ppm)	10	10	<10	5	2	1	<1

SECTION VII

EXPERIMENTAL PROCEDURES

Solution Preparation

As discussed in an earlier section, all detergent solutions used in corrosion studies were based on the basic granular detergent formulation:

50 weight percent total of STPP or NTA or both
20 weight percent LAS
18 weight percent fillers
6 weight percent sodium silicate (1.6:1 SiO_2 to Na_2O ratio)
6 weight percent water

From the supplied LAS solution (27.4 weight percent weight percent LAS, 24.1 weight percent fillers and 48.5 weight percent water), sodium silicate solution (43 weight percent sodium silicate, 57 weight percent water), STPP and NTA salts, 2 weight percent stock solutions of the following detergent formulations were prepared using distilled water.

Stock Solution 'A' - 2 Weight Percent of 50 Weight Percent STPP-Based Detergent

50 weight percent STPP
20 weight percent LAS
18 weight percent fillers
6 weight percent sodium silicate (1.6:1 SiO_2 to Na_2O ratio)
6 weight percent water

Stock Solution 'B' - 2 Weight Percent of 50 Weight Percent NTA-Based Detergent

50 weight percent NTA
20 weight percent LAS
18 weight percent fillers
6 weight percent sodium silicate (1.6:1 SiO_2 to Na_2O ratio)
6 weight percent water

Stock Solution 'C' - 2 Weight Percent Solution of 37.5 Weight Percent STPP - 12.5 Weight Percent NTA-Based Detergent

37.5 weight percent STPP
12.5 weight percent NTA
18 weight percent fillers
6 weight percent sodium silicate (1.6:1 SiO_2 to Na O ratio)
6 weight percent water

150 ml aliquots of 0.06, 0.12, and 0.18 weight percent solutions were prepared for corrosion studies from the above 2 weight percent stock solutions by dilution of 4.5, 9.0, and 13.5 ml samples to 150 mils respectively. The dilutions were made with water of either 15 or 150 ppm hardness.

The waters of 15 and 150 ppm hardness were prepared as stock solutions from a 3:1 mixture of $CaCl_2$ to $MgCl_2$ in distilled water.

Corrosion-Coupon Preparation and Exposure

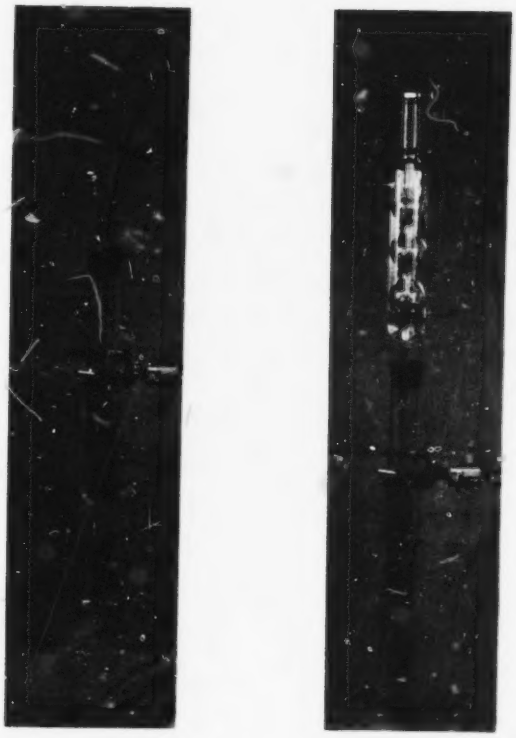
Coupons of size 2 x 3/4 in. and thickness between 0.020 and 0.125 in. for the various metals were prepared for the corrosion studies. The coupons contained a 1/4 in.-diameter hole near one end. Coupons were abraded to a '400' metallographic paper finish with the exception of 1100 Aluminum coupons which were abraded to a '600' metallographic paper finish. Each coupon was stamped with an identifying letter and number according to the following designation (Table 2).

Table 2. Coupon Identification

Metal	Identifying Coupon Letter
1100 Aluminum	A
260 Brass	B
Electrolytic Copper	C
Die-Cast Zinc	D
Nickel	E
Type 304 Stainless Steel	F
Type 420 Stainless Steel	G
1020 Carbon Steel	H
Chemical Lead	L
Cast Iron	M

Prior to exposure, the coupons were degreased with acetone and weighed to the nearest 0.1 mg.

Corrosion coupons were exposed to detergent formulations in 16-in. long x 1-1/4-in. diameter tubes. A typical tube setup is shown in Figure 1a for the 130 F temperature studies and in Figure 1b for the 160 F temperature studies. In both setups, two coupons were supported on glass hooks attached to a central glass tube. The glass tube, in addition to aiding support of the coupons, allowed the introduction of compressed air into the tubes for continuous aeration and mild agitation of the solutions. Outlets were provided at the top of the tubes for the air. As shown in Figure 1b the tubes for 160 F temperature studies included water condensers to prevent the loss of solution due to evaporation. Condensers were not required for the studies at 130 F. Each tube employed 150 ml of detergent solution which was sufficient to cover the coupons by several inches.



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a b

FIGURE 1. TYPICAL TUBE SETUPS FOR (a) 130 F and (b) 160 F CORROSION STUDIES

Temperature was controlled at 130 and 160 F by containing the tubes within aluminum blocks (18 x 18 x 18 in.). The aluminum blocks contained cylindrical holes to support the tubes in an upright position with about 4 inches of the tubes exposed above the top of the blocks. Heating of the blocks was readily conducted by attachment of bar heating elements to the sides of the blocks. The temperatures of the solustions were, therefore, readily controlled to within ±1F using standard temperature-control units.

Coupons were exposed for 2, 5, 11, and 14 days, depending upon the metal, and in all cases the solutions were continuously aerated by the bubbling through of air which also provided mild agitation. To prevent contamination of solutions with other metals, special attention was made to use each tube with only one type of metal under study.

Coupon Descaling and Corrosion Evaluation

To evaluate corrosion of coupons by weight-loss, it was necessary to descale the exposed specimens. Many of the adopted descaling procedures were recommended practice.[3] The procedures are outlined in Table 3.

Table 3. Coupon-Descaling Procedures

Metal	Descaling Procedure	Number of Treatments	Blank, mg/ treatment
1100 Aluminum	2-minute immersion in 75 weight percent HNO_3	1	< 0.1
260 Brass	3-minute immersion in 10 weight percent H_2SO_4. Light scrub with bristle brush under running water.	1	0.2
Electrolytic Copper	3-minute immersion in 10 weight percent H_2SO_4	1	0.2
Die-Cast Zinc	10-minute immersion in 10 weight percent NH_4Cl at 140 F. Scrub with bristle brush under running water.	2	0.8
1020 Carbon Steel	10-minute immersion in 15.5 volume percent H_3PO_4 inhibited with 1.55 volume percent Rodine 82-A (AmChem Products, Inc.) at 140 F. Scrub with bristle brush under running water.	2	0.8
Chemical Lead	5-minute immersion in 5 weight percent ammonium acetate at 140 F. Scrub with bristle brush under running water.	3	2.0
Cast Iron	2-minute immersion in 15.5 volume percent H_3PO_4 inhibited with 1.55 volume percent Rodine 82-A (AmChem Products, Inc.) at room temperature. Scrub with bristle brush under running water.	2	1.9

As seen from Table 3, blanks were generally small but did allow correction for metal loss during descaling procedures. After descaling, the coupons were rinsed with water, washed with acetone, dried and reweighed to determine weight loss.

The corrosion rates in terms of milligrams per (decimeter)^2 per day (mdd) were determined from the weight-loss data using the relationship

$$CR\ (mdd) = \frac{100\ W}{AT} \qquad (1)$$

where CR (mdd) = corrosion rate in mdd
W = weight loss in mg
A = total coupon area in cm^2
T = duration of exposure in days.

The corrosion rate in mdd was converted to corrosion rate expressed in mils penetration per year (mpy) according to the relationship

$$CR\ (mpy) = 3.94 \times 10^{-3}\ CR\ (mdd) = \frac{0.394\ W}{ATD} \qquad (2)$$

where CR (mpy) = corrosion rate in mpy
D = density in g/cm^3.

Table 4 gives the areas of the various metal coupons, the density of the metals and the conversion factors from mdd to mpy. The difference in area between the coupons was due to the difference in sheet thickness of the metals.

After descaling procedures had been completed and corrosion rates calculated, the coupons were examined metallographically.

Table 4. Coupon-Corrosion-Rate Factors

Metal	Coupon Area, cm^2	Density, g/cm^3	Multiply mdd By These Factors To Obtain mpy
1100 Aluminum	19.42	2.72	0.528
260 Brass	19.79	8.52	0.169
Electrolytic Copper	19.79	8.94	0.161
Die-Cast Zinc	21.35	7.13	0.202
1020 Carbon Steel	19.95	7.85	0.183
Chemical Lead	21.17	11.33	0.127
Cast Iron	20.85	7.20	0.183

Electrode Preparation and Electrochemical Measurements

A limited number of electrochemical corrosion-rate studies have been conducted in the detergent formulations to establish corrosion rates on the less-corrosive materials and to determine the dependency of corrosion rate upon exposure time. For these studies, electrodes of the metals, tabulated in Table 1, were prepared. The corrosion rates were determined using the linear polarization method.

Electrodes for the electrochemical studies were prepared using Kold-Weld Resin (Precision Dental Manufacturing Company, Chicago, Illinois). Coupons 2 x 3/4 in. were mechanically attached to a copper rod and the assembly placed in a mould from which electrodes, as shown in Figure 2, were cast using the cold-setting resin. The exposed area of the electrodes was 9/8 in.^{2} (7.2 cm^2). Duplicate electrodes were used with electrode areas facing each other 1 in. apart in 250-ml beakers containing 150-ml aliquots of the detergent formulations. The electrodes were shorted during periods of no measurement. Continuous aeration and mild agitation in each cell was provided by the entry of air through a glass tube. The cells were maintained at 130 ±1 F during experiments by continuous immersion in a water bath controlled at this temperature.

Figure 3 shows the electrical circuit for conducting the electrochemical corrosion-rate measurements using the linear polarization method. DC power was provided by a 1-1/2-volt dry battery across a 1-ohm potentiometer 'A' in series with a 68-ohm resistor. A portion of the voltage across potentiometer 'A' was fed across the poles of a DPDT microswitch in parallel with a series of circuits containing the electrochemical cell and a rotary switch 'B' with a choice of 1, 10, 100, and 1000-ohm resistors. The microswitch was activated by a cam attached to a continuously variable speed motor such that dc power to the electrochemical cell could be reversed for times up to every 3 minutes. By adjustment of the potentiometer 'A' a steady and reversible 10-mV signal (ΔE) could be imposed across the terminals of the electrochemical cell. The current (ΔI) flowing through the cell was measured by the voltage drop across the selected resistor in the rotary switch 'B'. This voltage drop was fed to a sensitive recorder (Honeywell, Electronik 19). Figure 4 shows the types of records obtained with this method for general corrosion and localized or pitting corrosion. As shown in Figure 4, a symmetrical current was measured upon voltage reversal for general corrosion. However, for localized corrosion, the establishment of different corrosion potentials on each electrode leads to a galvanic current through the cell and assymetry in the measured current through the cell upon voltage reversal.

The linear polarization method of corrosion rate measurement is based upon the linear relationship between ΔE and ΔI at small values of ΔE of the order of 10mV. ΔE and ΔI are related to the corrosion rate I_C through the relationship

$$I_C = \frac{b_A b_C}{2.3\ (b_A + b_C)} \cdot \frac{\Delta I}{\Delta E} \qquad (3)$$

where b_A and b_C are Tafel slopes for the anodic and cathodic reactions respectively of the corrosion process.[4] The values of b_A and b_C can be determined from potentiodynamic polarization curves of the metals in the detergent solutions. Using the recommended potentiodynamic polarization method[5], the potential of the electrode was varied continuously with respect to a saturated calomel reference electrode at a preset rate utilizing a potentiostat (Anotrol, Model 4100), a scanner control (Magna, Model 4510) and x-y recorder (Honeywell, Model 520) with a logarithmic voltmeter/amplifier (Hewlett Packard, Model 7563A). The potentiodynamic curves were determined at present rates between 1.2 and 1.6 volt per hour.

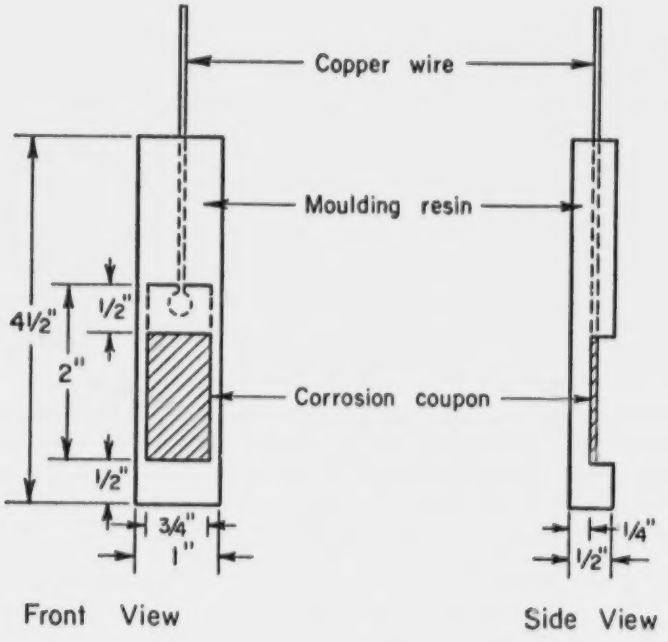


FIGURE 2. ELECTRODE FOR ELECTROCHEMICAL MEASUREMENTS

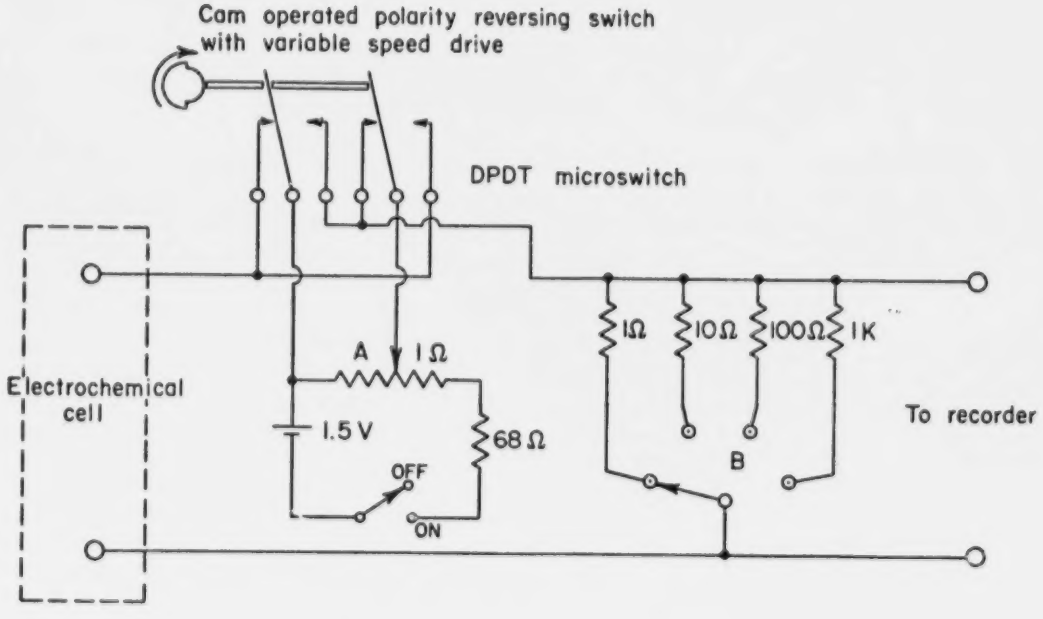
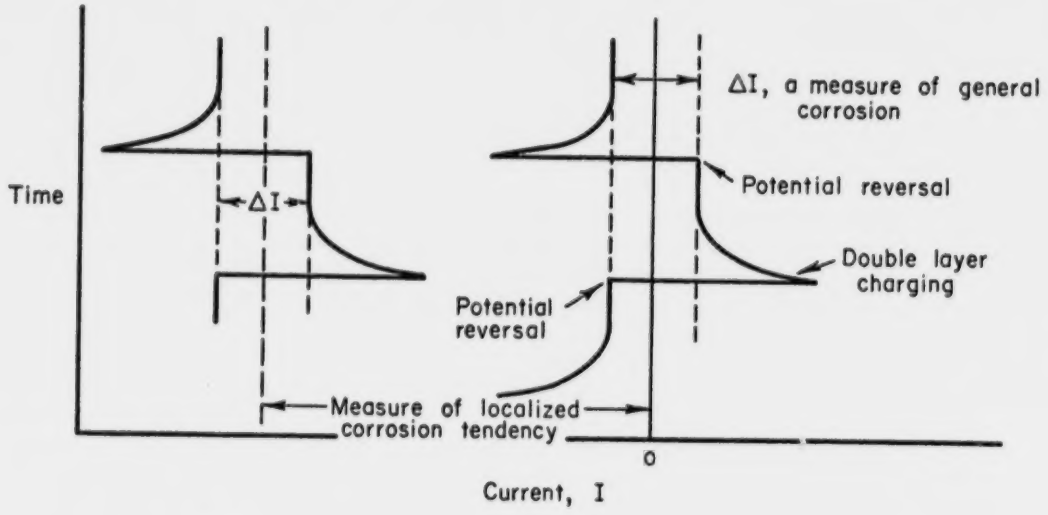


FIGURE 3. ELECTRICAL CIRCUIT FOR ELECTROCHEMICAL LINEAR-POLARIZATION MEASUREMENTS



a. Localized Corrosion

b. General Non-Localized Corrosion

FIGURE 4. SCHEMATIC OF LINEAR POLARIZATION MEASUREMENTS

For metals showing a passive anodic behavior, b_A approaches infinity and Equation 3 approximates to Equation 4.

$$I_C = \frac{b_C}{2.3} \cdot \frac{\Delta I}{\Delta E} \quad . \tag{4}$$

For systems showing a limiting cathodic current behavior as in diffusion-controlled reactions, b_C approaches infinity and Equation 3 approximates to Equation 5.

$$I_C = \frac{b_A}{2.3} \cdot \frac{\Delta I}{\Delta E} \tag{5}$$

SECTION VIII

EXPERIMENTAL RESULTS

Experimental work has been conducted on a variety of materials in a number of detergent solutions with the employment of both coupon-weight loss and electrochemical "linear polarization" corrosion evaluation methods. The experimental results of this work are presented for each material.

1100 Aluminum

The coupon-weight-loss data for 1100 Aluminum are tabulated in Tables 5 and 6 for STPP and NTA detergents, respectively. Weight losses on this metal varied between 0.8 and 10.8 mg per coupon for exposure periods of 11 to 14 days. In general, the corrosion rates were low and ranged between 0.20 and 2.7 mils per year. As indicated in Tables 5 and 6, the metal generally suffered general corrosion but in several experiments pitting was noted adjacent to the support holes in the coupons. Due to the absence of pits in other areas, it was concluded that such pitting was probably associated with contamination of the material near the support hole from drilling operations.

Figure 5 summarizes the weight-loss data in solutions at 130 F. It was apparent from Figure 5 that in both NTA- and STPP-based detergents, the corrosion rates increased almost linearly with increase of concentration from 0.06 to 0.18 weight percent. In both detergent formulations, the soft-water condition was slightly more corrosive by about 0.5 mil per year or 50 percent at all concentrations, and the NTA solution was marginally the most corrosive. The effect of increasing temperature from 130 to 160 F in 0.12 weight percent solution of 150-ppm hardness was to slightly increase corrosion. However, in 15-ppm hardness, the effect was not significant.

The increased corrosivity of NTA solutions over STPP solutions was more readily seen by the representation of the data as shown in Figure 6. The increased corrosivity factors are summarized in Table 7.

As seen from Table 7, there was an increased corrosivity factor of 1.1 in all detergent concentrations in the soft-water condition. Although, there was no increased corrosivity in 0.06 and 0.12 weight percent solutions in the hard-water condition, the corrosivity factor was maximum at 1.3 in the 0.18 weight percent detergents. The increased corrosivity factor, therefore, varied between 1.0 and 1.3 for 1100 Aluminum at 130 F solution conditions.

Table 5. Coupon-Weight Loss Data for 1100 Aluminum in 50 Weight Percent STPP-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate(a) mdd	mpy	Remarks
0.06	15	A45	130	11	1.5	0.79	Bright appearance. A few pits near support hole.
		A46	130	11	1.4	0.74	
	150	A47	130	11	0.37	0.20	Dull gray. A few pits near support hole.
		A48	130	11	0.47	0.25	
0.12	15	A22	160	14	2.32	1.22	Bright with slight reddish-green lustre.
		A23	160	14	2.61	1.38	
		A18	130	14	2.91	1.54	Bright metallic appearance.
		A19	130	14	2.39	1.26	
	150	A24	160	14	1.91	1.01	Bright with slight reddish-green lustre. A few pits near support hole.
		A29	160	14	1.43	0.76	
		A20	130	14	1.58	0.83	Bright with reddish-green lustre. A few pits near support hole.
		A21	130	14	1.66	0.88	
0.18	15	A25	130	11	3.79	2.00	Metallic lustre. General corrosion.
		A26	130	11	4.45	2.35	
	150	A27	130	11	2.95	1.56	Metallic lustre. General corrosion.
		A28	130	11	3.18	1.68	

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

Table 6. Coupon Weight Loss Data for 1100 Aluminum in 50 Weight Percent NTA-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate[a] mdd	mpy	Remarks
0.06	15	A41	130	11	1.8	0.95	Reddish-green lustre.
		A42	130	11	1.5	0.79	General corrosion.
	150	A43	130	11	0.42	0.22	Dull gray. A few pits
		A44	130	11	0.37	0.20	near support hole.
0.12	15	A9	160	14	3.09	1.63	Dull gray. General corrosion
		A10	160	14	2.76	1.46	with a few pits (2-4 mils deep) near support hole.
		A16	130	14	3.09	1.63	Dull gray. General corrosion
		A17	130	14	2.65	1.40	with pits (2-4 mils deep) near support hole.
	150	A11	160	14	2.28	1.20	Dull gray. General corrosion
		A12	160	14	2.54	1.34	with a few pits (2 mils deep) near support hole.
		A13	130	14	1.65	0.87	Dull gray. General corrosion
		A14	130	14	1.62	0.86	with a few pits (2 mils deep) near support hole.
0.18	15	A30	130	11	4.49	2.37	Dull reddish-green film.
		A31	130	11	5.05	2.67	General corrosion.
	150	A32	130	11	3.60	1.90	Dull reddish-green tarnish
		A33	130	11	4.12	2.18	film. Few pits near support hole.

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

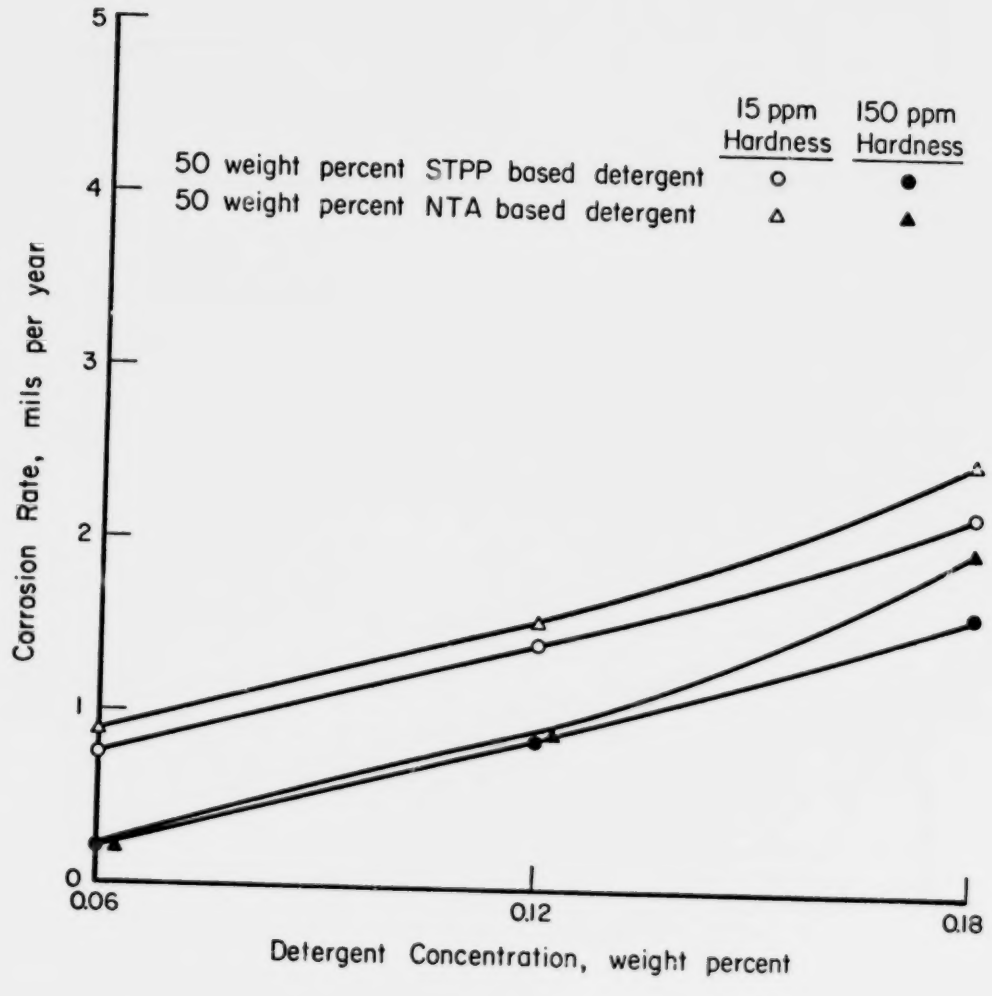


FIGURE 5. CORROSION RATE OF 1100 ALUMINUM AS A FUNCTION OF DETERGENT CONCENTRATION IN 15 PPM AND 150 PPM WATER HARDNESS AT 130 F

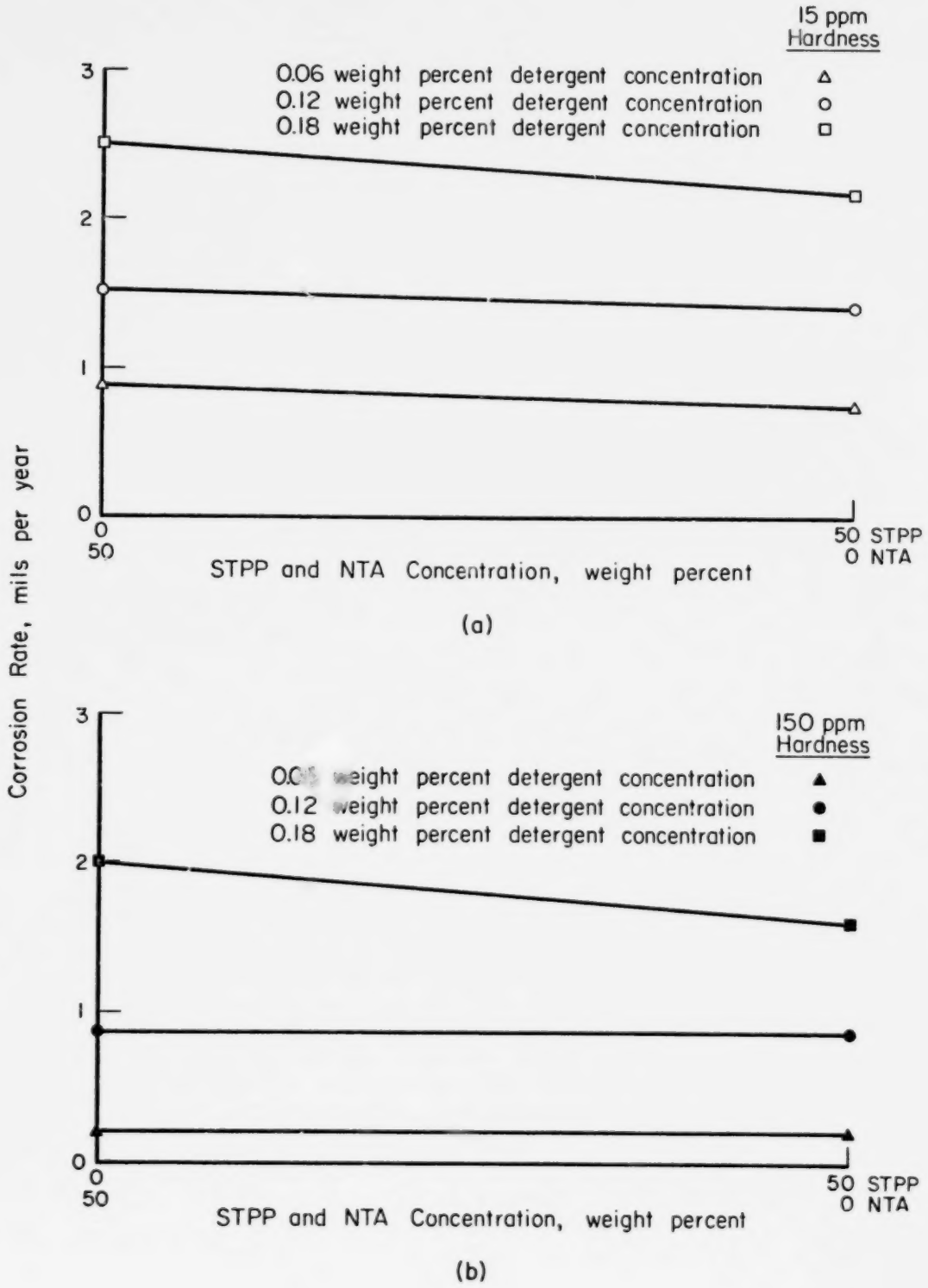


FIGURE 6. CORROSION RATE OF 1100 ALUMINUM AS A FUNCTION OF STPP AND NTA CONCENTRATION AT (a) 15 PPM AND (b) 150 PPM WATER HARDNESS AND 130 F

Table 7. Increased Corrosivity Factors for NTA Solutions Over STPP Solutions with 1100 Aluminum

Detergent Concentration, weight percent	15-ppm Hardness	150-ppm Hardness
0.06	1.1	1.0
0.12	1.1	1.0
0.18	1.1	1.3

The corrosion behavior of 1100 Aluminum in a number of 0.12 weight percent solutions at 130 F was measured by the electrochemical linear polarization method. Results are shown in Figures 7(a) and 7(b). The data indicated that in all solutions, corrosion was initially high (5 to 30 mils per year) but decreased considerably within a 1-day exposure. Between 1 and 3 days, the corrosion rates became steady at values between 0.04 and 0.4 mil per year. The decrease in corrosion rate with time paralleled a decrease in corrosion potential from about -1.1 volt to -0.4 volt versus saturated calomel electrode (SCE). The data in Figures 7(a) and 7(b) indicated that no major differences occurred in corrosion rate with the use of a mixed detergent; i.e., 37.5 STPP-12.5 NTA-based detergent compared to a pure 50 STPP- or 50 NTA-based detergent.

The corrosion rates in Figure 7 were obtained using Equation 4 with values of $b_A = \infty$ and $b_C = 0.14$ volt as determined from polarization curves in STPP and NTA solutions. Values of I_C were converted to mils per year using the relationship $1\ \mu\ A/cm^2 = 0.43$ mpy. It is apparent that corrosion rates evaluated by the linear polarization method were about an order of magnitude smaller than values determined by the weight-loss method. This difference is not accounted for by even drastic changes in b_A or b_C values but appears to be associated with the development of a poorly conducting film on 1100 Aluminum. The presence of the film causes a low assessment of the corrosion rates by the electrochemical method.

260 Brass

Weight-loss data for 260 Brass in STPP and NTA detergents are presented in Tables 8 and 9 respectively. Weight losses varied between 1.1 and 18.3 mg per coupon for exposure times of 5 days. Corrosion rates were low (between about 0.2 and 3 mils per year). In many experiments, the material tarnished and a wide variety of colored films were produced. Although corrosion was always general and no pitting corrosion was observed, some dezincification of the material in some environments was apparent. The dezincification was noted by the copper color of the dezincified coupons after descaling. The copper color of the coupons was not the result of deposition of copper from the descaling solution of 10 weight percent H_2SO_4 or dezincification produced by the descaling solution as concluded from parallel studies with unexposed brass coupons. The dezincification process appeared to be associated more with the STPP-based

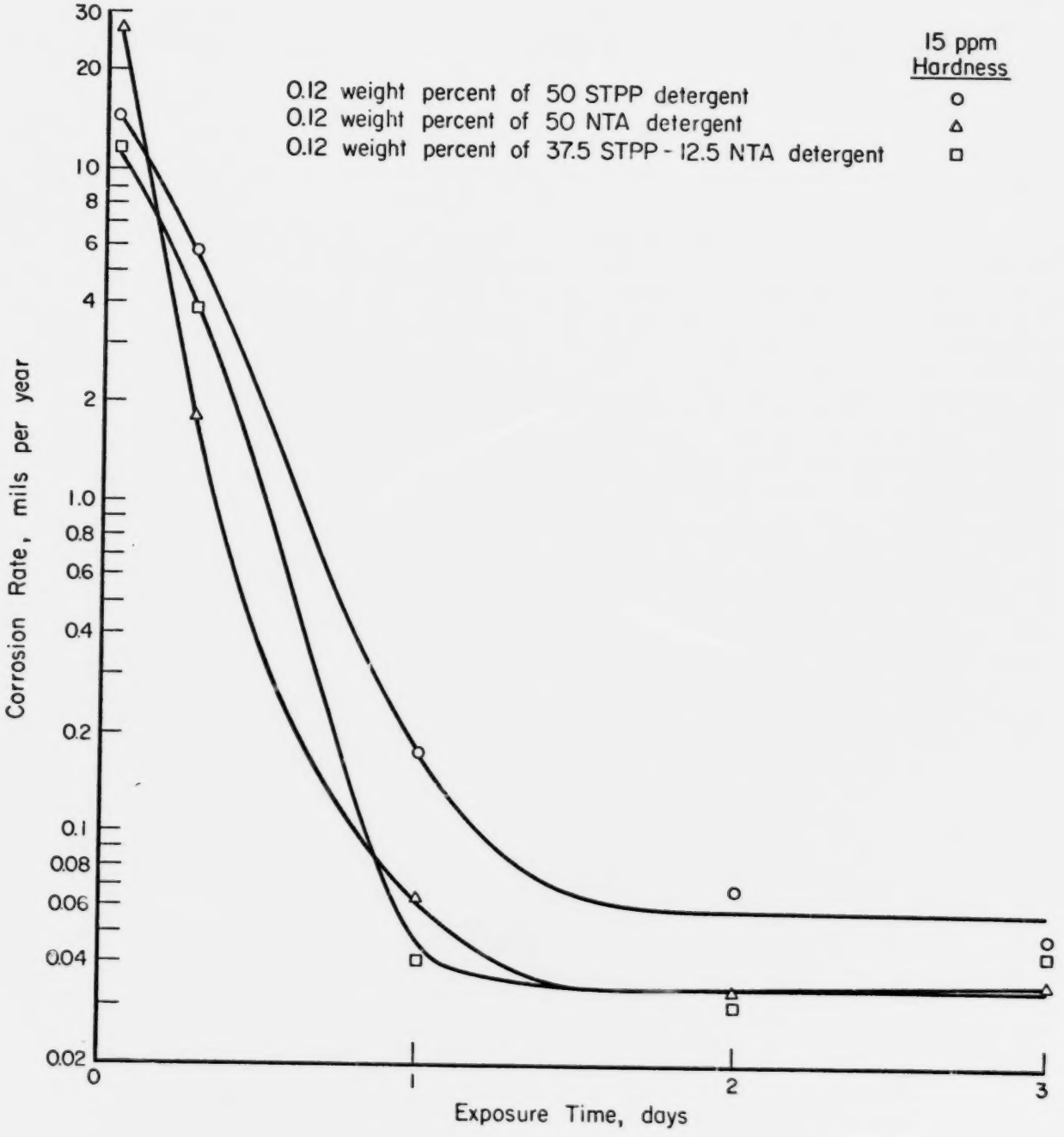


FIGURE 7(a). CORROSION RATE OF 1100 ALUMINUM AS A FUNCTION OF EXPOSURE TIME IN 15 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

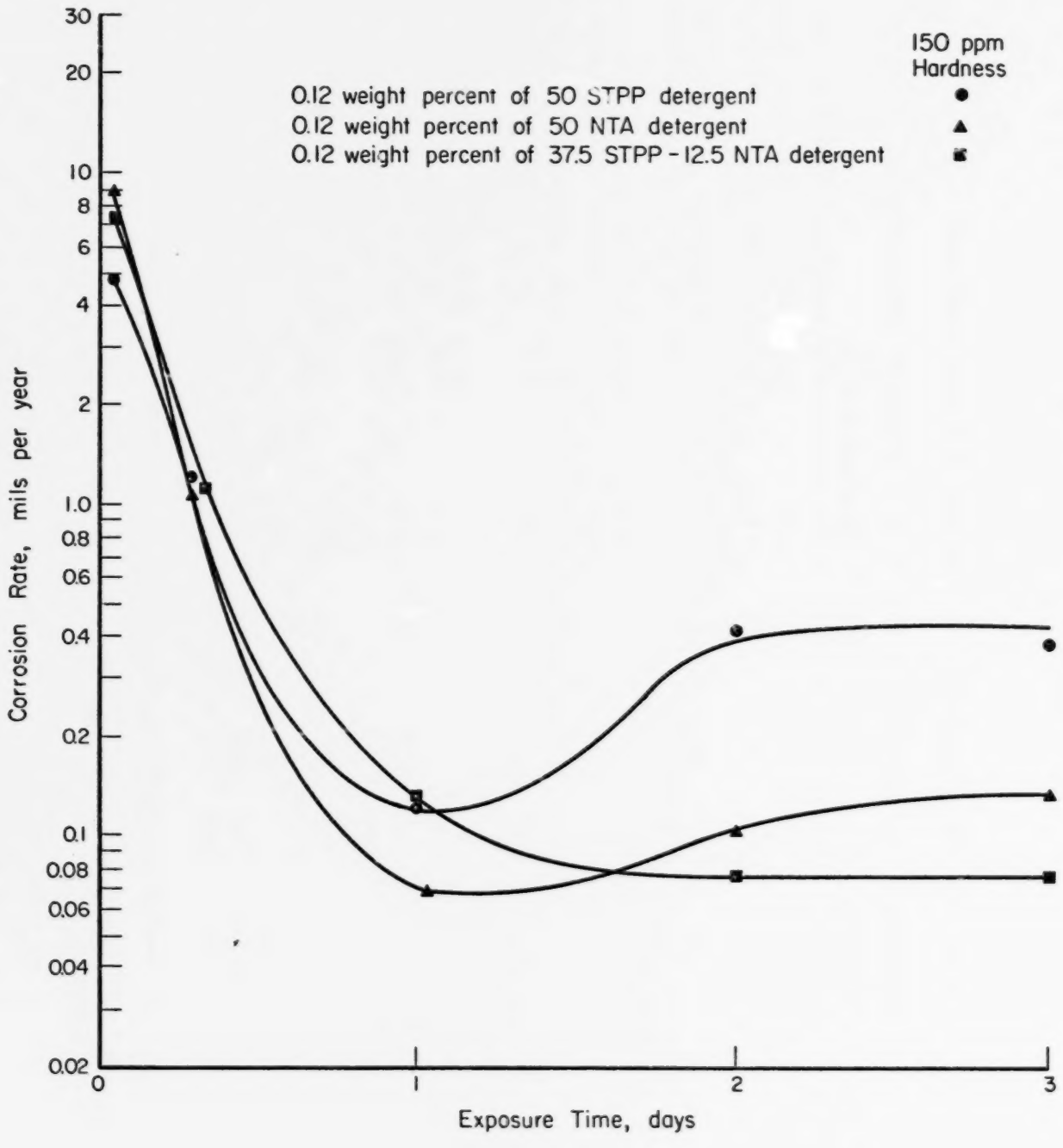


FIGURE 7(b). CORROSION RATE OF 1100 ALUMINUM AS A FUNCTION OF EXPOSURE TIME IN 150 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

Table 8. Coupon-Weight-Loss Data for 260 Brass in 50 Weight Percent STPP-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp F	Exposure, days	Corrosion Rate(a) mdd	mpy	Remarks
0.06	15	B45	130	5	5.0	0.85	Silver tarnish film. Moderate dezincification indicated after descaling.
		B46	130	5	4.4	0.74	
	150	B47	130	5	1.1	0.19	Purple and gold tarnish film. No apparent dezincification.
		B48	130	5	1.1	0.19	
0.12	15	B11	160	5	6.4	1.08	Green tarnish film. General corrosion with dezincification.
		B12	160	5	6.2	1.05	
		B13	130	5	8.4	1.42	Blue tarnish film. General corrosion with greater dezincification.
		B14	130	5	7.5	1.27	
	150	B21	160	5	2.7	0.46	Green tarnish film. General corrosion.
		B22	160	5	2.9	0.49	
		B23	130	5	4.9	0.83	Blue tarnish film. General corrosion and dezincification.
		B24	130	5	4.5	0.76	
0.18	15	B25	130	5	11.4	1.93	Blue tarnish film. Showed brownish color due to dezincification after descale.
		B26	130	5	11.5	1.94	
	150	B27	130	5	7.7	1.30	Blue tarnish film. Showed brownish color due to dezincification after descale
		B28	130	5	8.6	1.45	

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

Table 9. Coupon-Weight-Loss Data for 260 Brass in 50 Weight Percent NTA-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp F	Exposure, days	Corrosion Rate[a] mdd	mpy	Remarks
0.06	15	B41	130	5	6.1	1.03	Purple tarnish film. A trace of dezincification indicated after descaling.
		B42	130	5	6.2	1.05	
	150	B43	130	5	5.9	1.00	Reddish-green tarnish film. Moderate dezincification indicated after descale.
		B44	130	5	6.2	1.05	
0.12	15	B9	160	5	14.0	2.37	Violet tarnish film. General corrosion.
		B10	160	5	14.1	2.38	
		B16	130	5	12.5	2.12	Green tarnish film. General corrosion.
		B17	130	5	11.5	1.94	
	150	B15	160	5	10.5	1.77	Black tarnish film. General corrosion.
		B18	160	5	11.3	1.91	
		B19	130	5	9.0	1.52	Reddish-blue tarnish film. General corrosion.
		B20	130	5	9.5	1.61	
0.18	15	B29	130	5	18.5	3.13	Dark green tarnish film. Showed pinkish color due to dezincification after descale.
		B30	130	5	16.6	2.81	
	150	B31	130	5	11.2	1.89	Light-green tarnish film. General corrosion. No dezincification
		B32	130	5	13.4	2.26	

[a] mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

detergents and occurs greatest at the 0.12 and 0.18 weight percent solutions. NTA-based solutions exhibited some mild dezincification at 0.06 and 0.18 concentrations but not at the 0.12 concentrations. The process occurrred in STPP solutions of pH 10.0 to 10.4 but not in the 0.06 STPP solution with 150 ppm hardness and pH 9.8. Since the process occurred in 0.06 NTA solutions of pH 9.9 and 10.3 for 150- and 15-ppm hardness, respectively, it appeared that the dezincification process might be associated in part with the solution pH range of about 9.9 to 10.4. The mild dezincification in the 0.18 NTA solution with 15 ppm hardness and pH 10.6 did, however, conflict since other solutions at pH 10.6 and 10.7 did not produce dezincification. As shown in Figure 8, metallography of the most dezincified material revealed that dezincification was limited only to a very thin surface film and did not penetrate into the subsurface layers of the material.

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FIGURE 8. CROSS SECTION OF DEZINCIFIED COUPON B14.
Note absence of subsurface corrosion.

Figure 9 summarizes the weight-loss data for 260 Brass. These data showed that, in all detergent solutions, the corrosion rate increased linearly with increase of detergent concentration. For both STPP and NTA solutions, the soft-water condition was more corrosive than the hard-water condition. NTA-based solutions in the soft-water condition were more corrosive than the other NTA and STPP solutions. As seen from Tables 8 and 9, the effect of an increase in temperature from 130 to 160 F in 0.12 weight percent

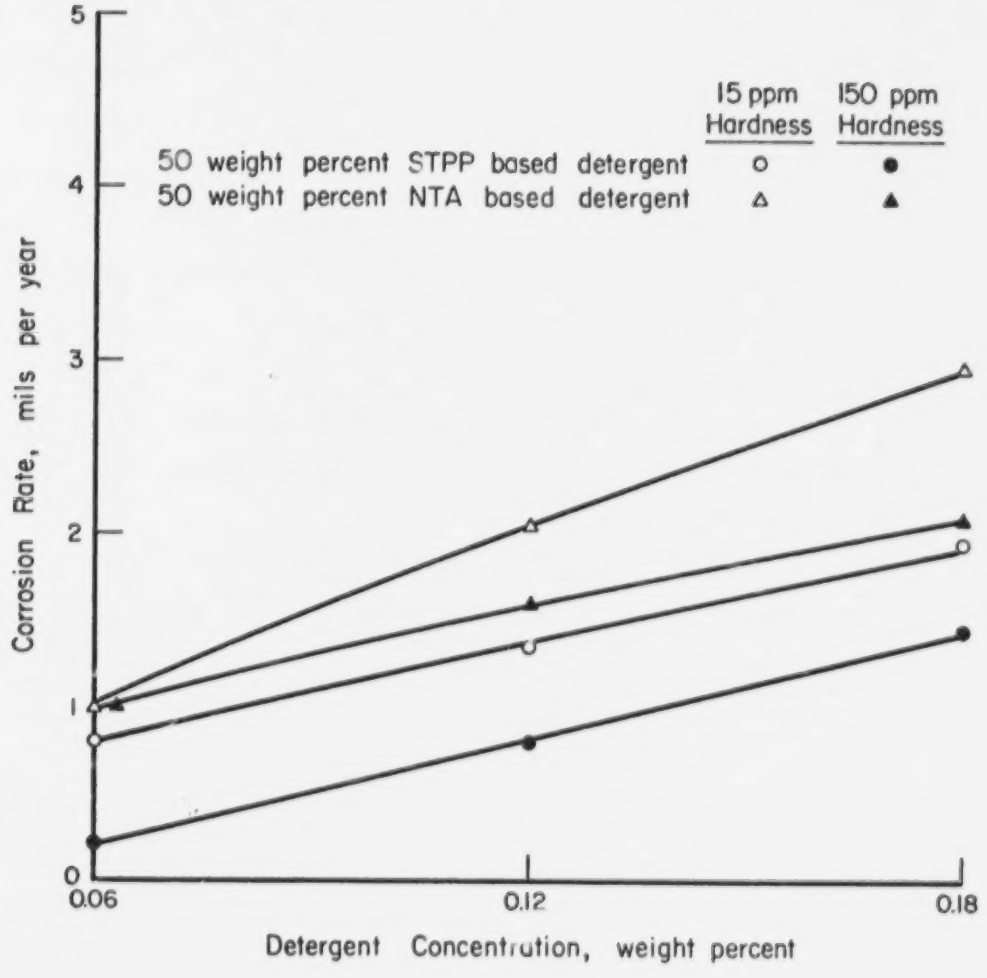


FIGURE 9. CORROSION RATE OF 260 BRASS AS A FUNCTION OF DETERGENT CONCENTRATION IN 15 PPM AND 150 PPM WATER HARDNESS AT 130 F

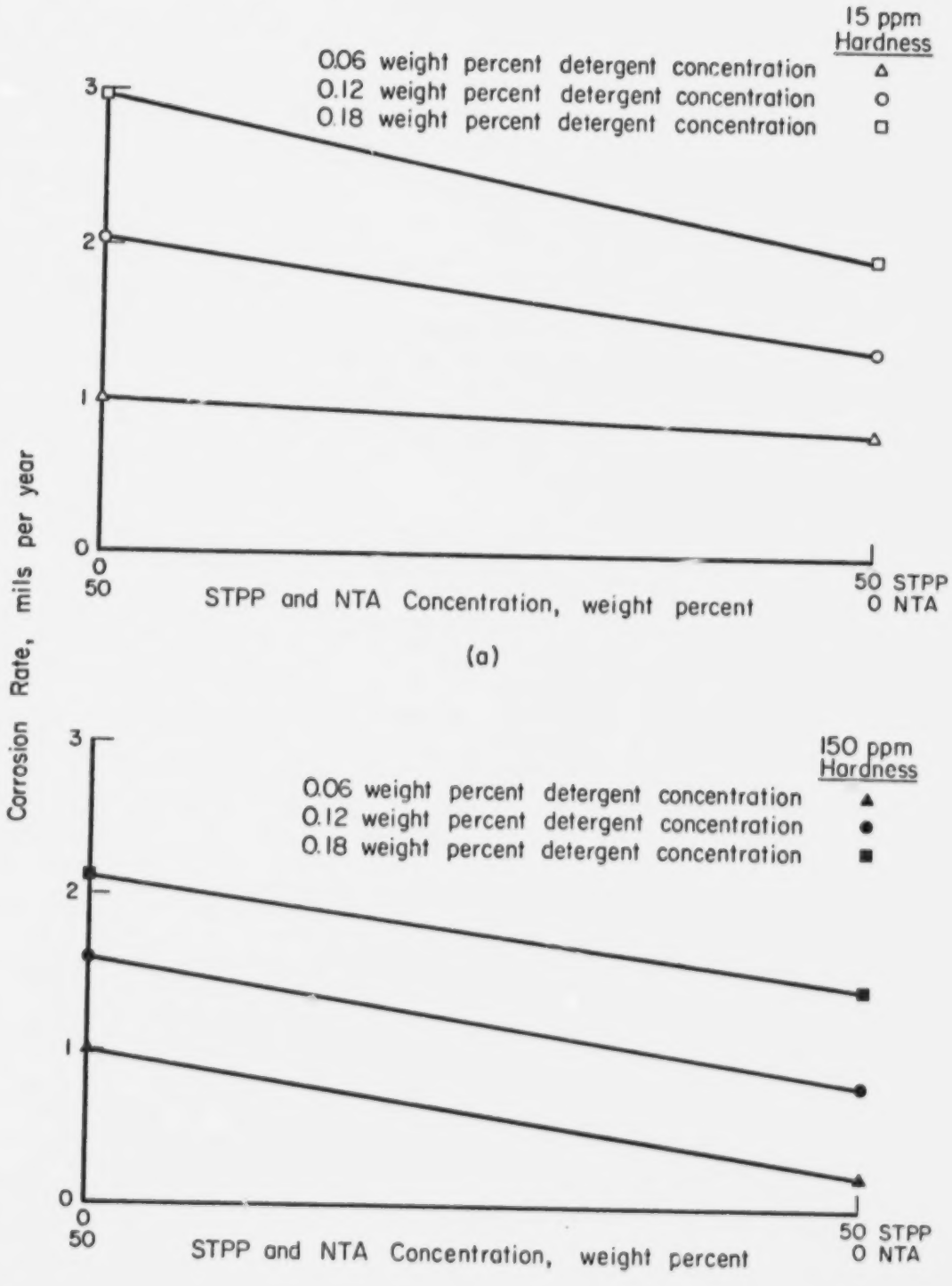


FIGURE 10. CORROSION RATE OF 260 BRASS AS A FUNCTION OF STPP AND NTA CONCENTRATION AT (a) 15 PPM AND (b) 150 PPM WATER HARDNESS AND 130 F

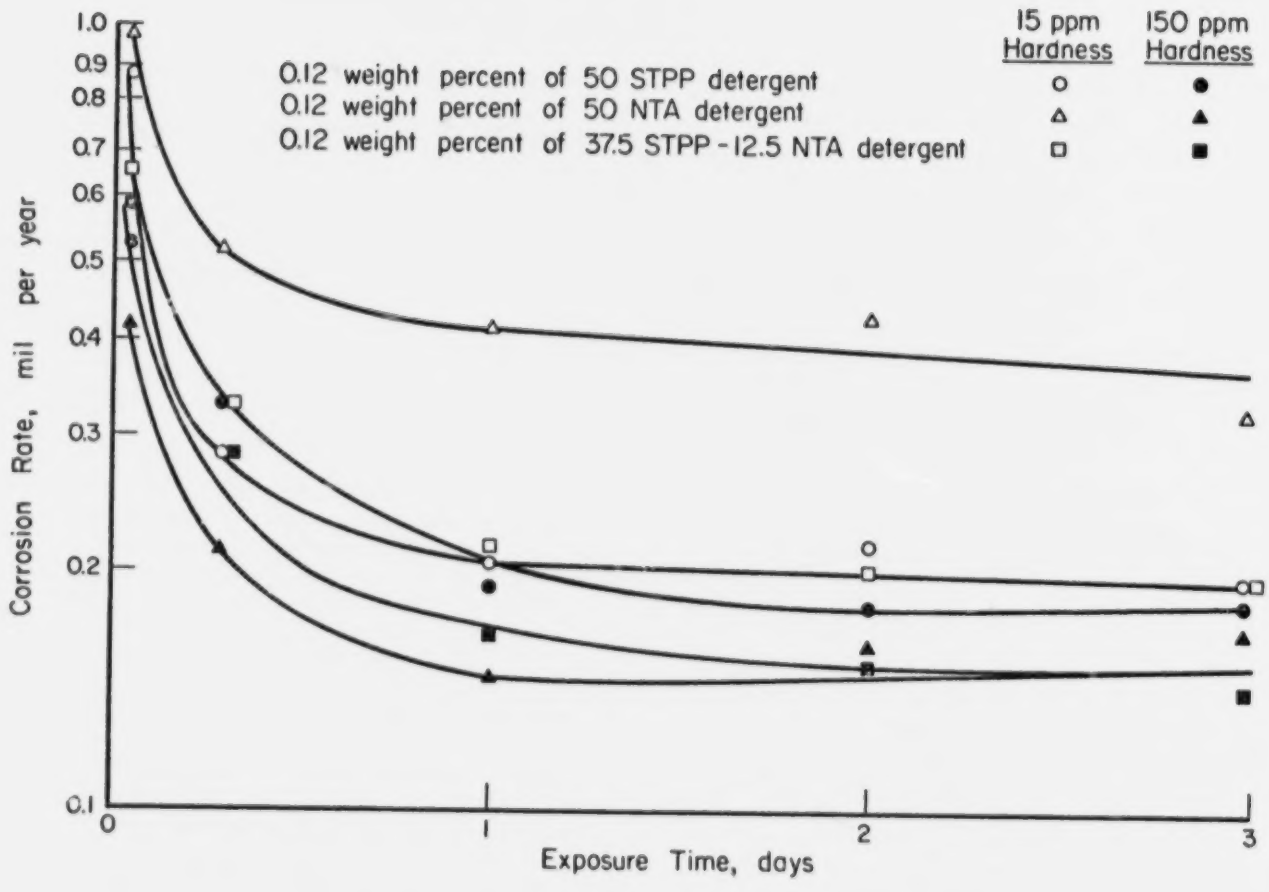


FIGURE 11. CORROSION RATE OF 260 BRASS AS A FUNCTION OF EXPOSURE TIME AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

solutions, was to cause a marginal increase in the rate of attack in NTA-based solutions, but, in STPP-based solutions a marginal decrease occurred. It is apparent from representation of the weight-loss data (Figure 10) that NTA-based solutions were more corrosive than the corresponding STPP solutions. As summarized in Table 10, the increased corrosivity factor was greatest in hard water solutions and reached a maximum value of 5.0 to 0.06 weight percent

Table 10. Increased Corrosivity Factors for NTA Solutions Over STPP Solutions with 260 Brass

Detergent Concentration weight percent	15-ppm Hardness	150-ppm Hardness
0.06	1.3	5.0
0.12	1.5	2.0
0.18	1.5	1.5

concentration. Thus, although there was no significant effect of concentration in soft water, the corrosivity factor increased with decrease of detergent concentration in hard water. The corrosivity factor varied between 1.3 and 5.0 on 260 Brass.

The corrosion data for 260 Brass using the linear polarization method is summarized in Figure 11. The results indicated that corrosion decreased considerably in the first day's exposure from about 1 to about 0.2 mil per year. The 0.12 weight percent NTA-based solution with soft water appeared the most corrosive. There was no marked difference in corrosion rate values between mixed detergents containing 37.5 STPP-12.5 NTA and the pure STPP and NTA-based detergents. Corrosion rates in Figure 11 were determined using Equation 4, since polarization curves indicated values of $b_A = \infty$ and $b_C = 0.20$ volt. Values of I_C were converted to mil per year using the relationship 1_μ A/cm^2 = 0.48 mpy. It was apparent from Figure 11 that calculated linear polarization corrosion rates were an order of magnitude smaller than corrosion rates determined from weight-loss data. Since drastic changes in b_A and b_C values could not account for this difference, it appeared that the developed tarnish film on these materials was sufficiently poorly conducting to cause a low assessment of the corrosion rate with the electrochemical method.

Electrolytic Copper

Coupon-weight loss data for electrolytic copper is summarized in Tables 11 and 12 for STPP and NTA detergents, respectively. Weight losses between

Table 11. Coupon-Weight-Loss Data for Electrolytic Copper in 50 Weight Percent STPP-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp F	Exposure, days	Corrosion Rate[a] mdd	mpy	Remarks
0.06	15	C45	130	5	3.4	0.54	Pale red tarnish film. General
		C46	130	5	3.4	0.54	corrosion.
	150	C47	130	5	1.6	0.26	Golden tarnish film. General
		C48	130	5	0.8	0.13	corrosion.
0.12	15	C11	160	5	2.1	0.34	Golden tarnish film. General
		C12	160	5	1.9	0.31	corrosion.
		C13	130	5	5.4	0.87	Golden tarnish film. General
		C14	130	5	6.5	1.1	corrosion.
	150	C21	160	5	3.4	0.55	Slight golden tarnish film.
		C22	160	5	2.0	0.32	General corrosion.
		C23	130	5	3.0	0.48	Golden tarnish film. General
		C24	130	5	3.0	0.48	corrosion.
0.18	15	C25	130	5	10.4	1.67	Golden tarnish film. General
		C26	130	5	9.4	1.55	corrosion.
	150	C27	130	5	10.2	1.64	Golden tarnish film. General
		C28	130	5	9.0	1.45	corrosion.

[a] mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

Table 12. Coupon-Weight-Loss Data for Electrolytic Copper in 50 Weight Percent NTA-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp F	Exposure, days	Corrosion Rate[a] mdd	mpy	Remarks
0.06	15	C41	130	5	5.9	0.95	Golden tarnish film. General corrosion.
		C42	130	5	5.3	0.85	
	150	C43	130	5	1.8	0.28	Golden tarnish film. General corrosion.
		C44	130	5	1.9	0.31	
0.12	15	C9	160	5	16.7	2.69	Golden tarnish film. General corrosion.
		C10	160	5	12.8	2.06	
		C17	130	5	11.7	1.88	Golden tarnish film. General corrosion.
		C18	130	5	11.9	1.92	
	150	C15	160	5	10.1	1.63	Golden tarnish film. General corrosion.
		C16	160	5	12.2	1.96	
		C19	130	5	10.9	1.75	Golden tarnish film. General corrosion.
		C20	130	5	10.8	1.74	
0.18	15	C29	130	5	17.0	2.74	Golden tarnish film. General corrosion.
		C20	130	5	17.4	2.80	
	150	C31	130	5	6.8	1.09	Golden tarnish film. General corrosion.
		C32	130	5	9.0	1.45	

[a] mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

1.2 and 17 mg per coupon were obtained over the 5-day exposure periods. Corrosion rates were generally low at values between 0.2 and 2.8 mils per year. As noted in Tables 11 and 12, the copper material usually showed a golden tarnish film after exposure, and corrosion appeared to be of a general nature.

Figure 12 summarizes the weight-loss data for experiments conducted at 130 F. It was clear that in all solutions, the copper corrosion rate increased as detergent concentration increased from 0.06 to 0.18 weight percent. The increase in corrosion rate was more marked in NTA solutions than in STPP solutions. The NTA solutions were more corrosive than the STPP solutions. The most corrosive solutions were those containing NTA and the soft water of 15-ppm hardness. From Tables 11 and 12, it appeared that an increase in temperature from 130 to 160 F in 0.12 weight percent NTA solutions had little effect upon the corrosion behavior. The same effect was noted in STPP solutions at the 150-ppm water hardness but in the 15-ppm water hardness, the increased temperature decreased the corrosion rate by almost a factor of 3. This temperature increase appears to have decreased corrosion probably through the production of a more protective tarnish film.

The weight-loss data as shown in Figure 13 indicated the NTA solutions were more corrosive than the corresponding STPP solutions. As summarized in Table 13, the increased corrosivity factor varied between 1.5 and 3.8. No marked change of corrosivity factor occurred with concentration in soft

Table 13. Increased Corrosivity Factors for NTA Solutions Over STPP Solutions with Electrolytic Copper

Detergent Concentration weight percent	15-ppm Hardness	150-ppm Hardness
0.06	1.8	1.5
0.12	1.9	3.5
0.18	1.7	3.8

water. However, in hard water the corrosivity factor increased with increase of detergent concentration.

The corrosion data for electrolytic copper using the linear polarization method is summarized in Figure 14. The data indicated that corrosion decreased rapidly within the first 1-day exposure from about 1 to 0.25 mil per year in all environments. Between 1 and 3 days, the calculated corrosion rates for all solutions were between 0.2 and 0.3 mil per year. It was apparent from these results that there was no marked difference in corrosion behavior between mixed detergents containing 37.5 STPP-12.5 NTA and the pure STPP and NTA detergents. Comparison of the linear polarization results with coupon weight-loss data indicated that the linear polarization corrosion rates were an order of magnitude lower. Values of $b_A = \infty$ and $b_C = 0.24$ volt were determined from polarization experiments and Equation 4 was employed to determine corrosion rates. The corrosion rate I_C was converted using the

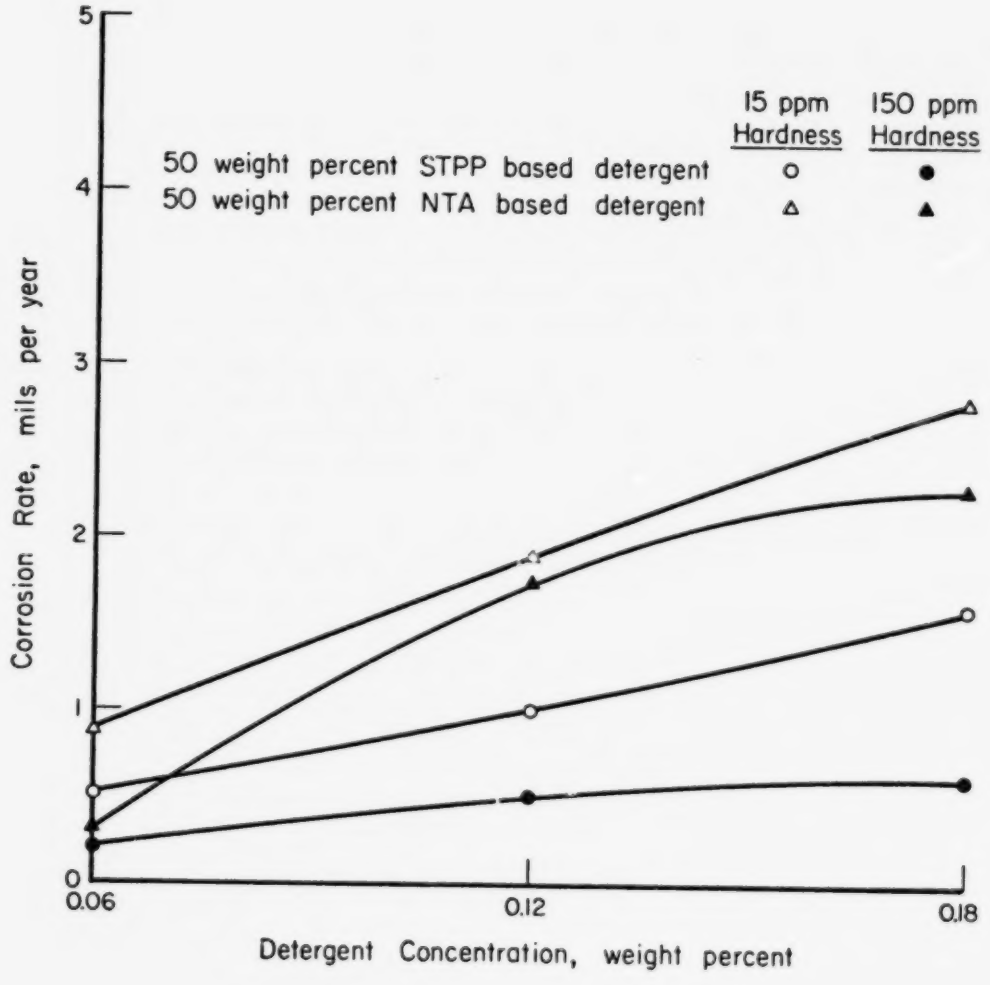


FIGURE 12. CORROSION RATE OF ELECTROLYTIC COPPER AS A FUNCTION OF DETERGENT CONCENTRATION IN 15 PPM AND 150 PPM WATER HARDNESS AT 130 F

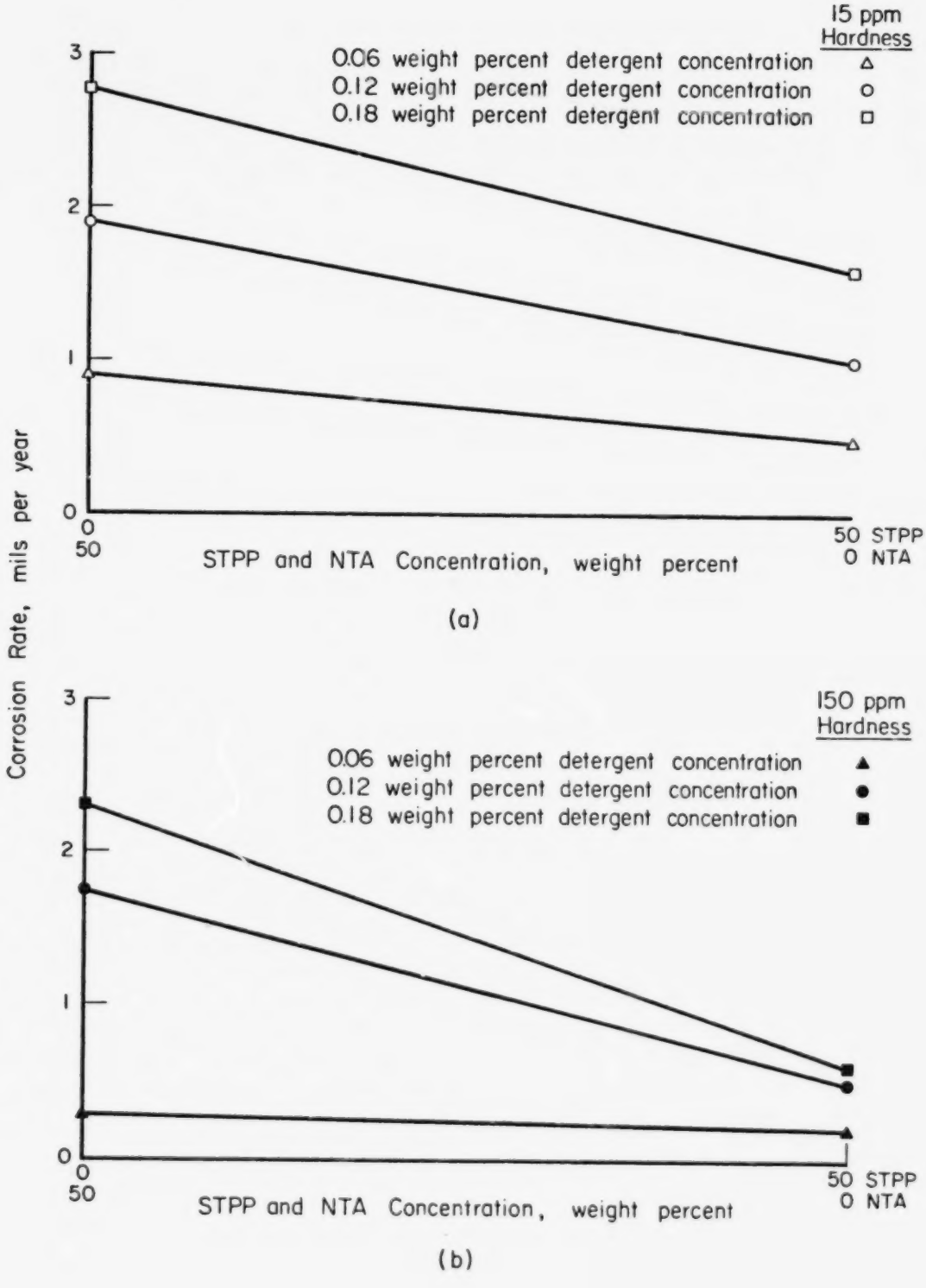


FIGURE 13. CORROSION RATE OF ELECTROLYTIC COPPER AS A FUNCTION OF STPP AND NTA CONCENTRATION AT (a) 15-PPM AND (b) 150-PPM WATER HARDNESS AND 130 F

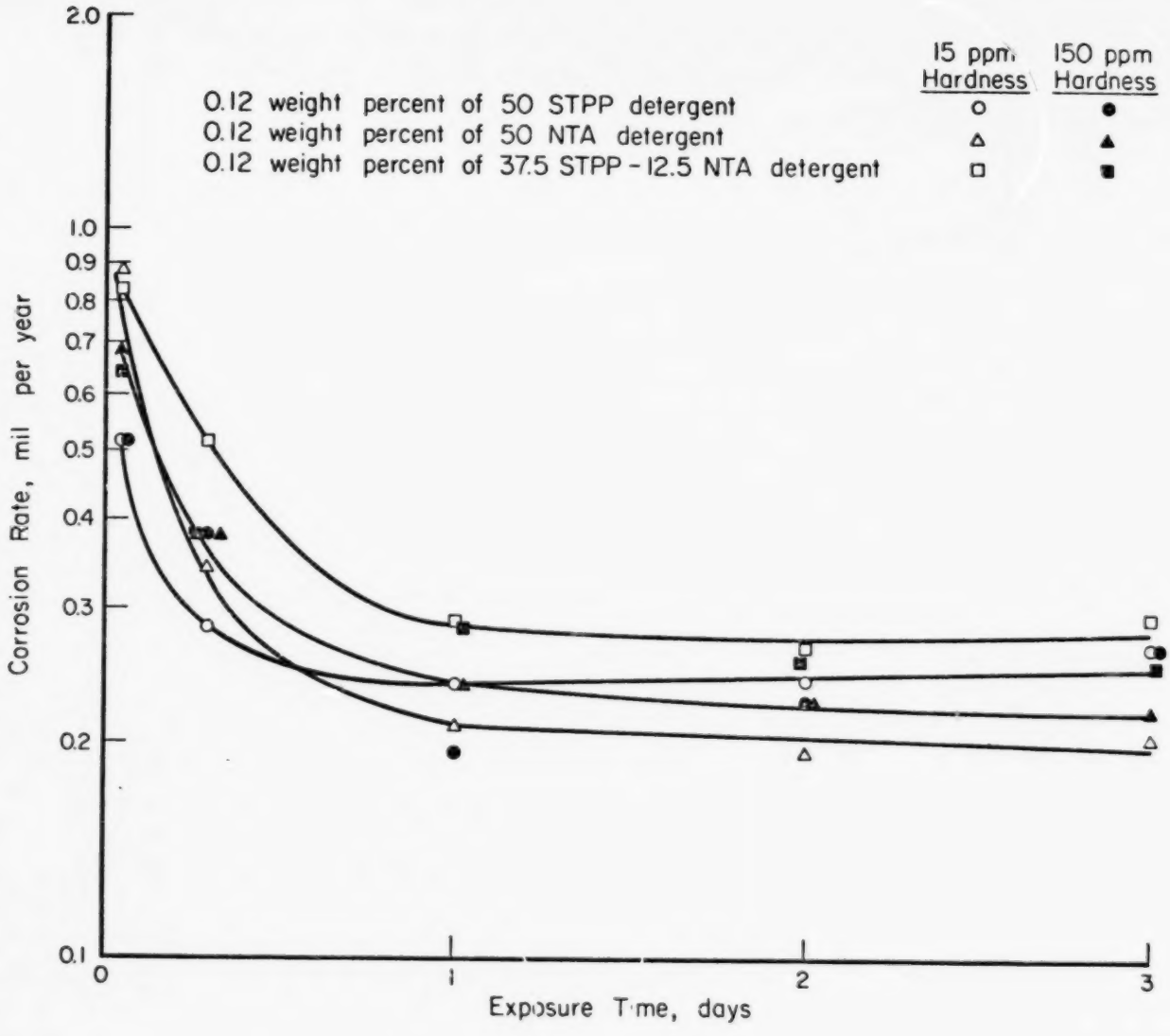


FIGURE 14. CORROSION RATE OF ELECTROLYTIC COPPER AS A FUNCTION OF EXPOSURE TIME AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

relationship 1 $\mu A/cm^2$ = 0.46 mpy. Since drastic changes in b_A and b_C values could not account for such differences between weight loss and electrochemical data, it appeared that poorly conducting tarnishing films developed on the copper electrodes caused a low assessment of linear polarization corrosion rates.

Die-Cast Zinc

Tables 14 and 15 summarize the coupon-weight-loss data for die-cast zinc in the STPP and NTA detergent solutions at 130 and 160 F. Weight losses were between 4.5 and 102 mg per coupon over the 2-day exposure periods to give both low and high corrosion rates between 2.1 and 44.3 mils per year. As shown by surface photographs of exposed coupons in Figures 15 to 18, a variety of features were obtained. In this material, general corrosion usually resulted in a continuous corrosion-product film on coupons (Figure 15) that sometimes was semivoluminous. Pitting corrosion of the order of 1 to 1-1/2 mils depth was usually associated with a moderate density of pitting corrosion deposits on the surface which were reasonably large and also slightly voluminous product (Figure 16). An example of such pitting corrosion is shown in the photomicrograph of Figure 19. It was evident from metallographic studies (Figure 19) that the pitting corrosion extended deeper (a factor of two) than surface optical measurements would reveal. A higher density of pitting corrosion deposits but of smaller size (Figure 17) generally indicated less aggressive pitting as evidenced in the photomicrograph of Figure 20. Corrosion of the die-cast zinc occurred in all solutions, but, as shown in Figure 18, the corrosion could be limited to mild low density pitting.

Figure 21, in which the weight-loss data are summarized, allows the effects of detergent concentration and water hardness to be more readily evaluated. In terms of overall weight loss, with the exception of the point at 0.18 weight percent NTA with 150-ppm water hardness, it is evident that the soft-water conditions of both NTA and STPP detergents were the most corrosive. Of these solutions, the most corrosive appeared to be the NTA-based solutions. The least overall corrosive solution appeared to be the STPP-based solutions with 150-ppm water hardness. Again with the exception of the point of 0.18 weight percent NTA and 150-ppm hardness, corrosion was maximum in 0.12 weight percent detergent concentrations. This behavior was contrary to results on aluminum, copper, brass, and lead in which corrosivity increased with increase of detergent concentration. It appears, therefore, that the slightly deeper but less dense pitting in 0.12 weight percent solutions was sufficient to cause greater weight loss than the less deep but sometimes more dense pitting in 0.06 and 0.18 weight percent solutions. As seen from Figure 21, however, at very large corrosion rates above 30 mils per year, the corrosion was general. Although severe pitting of 1 to 3 mils depth in 2 days in 0.12 percent solutions represents localized attack at a rate of 180 to 540 mils per year, it is doubtful that this rate would be sustained but rather would become stifled by its own corrosion product.

Table 14. Coupon-Weight-Loss Data for Die-Cast Zinc in 50 Weight Percent STPP-based Detergent

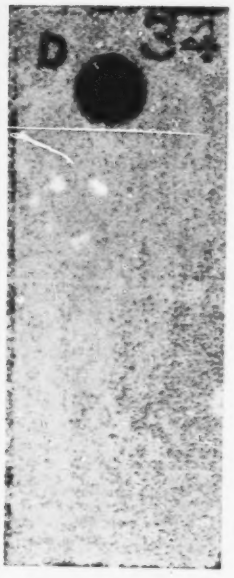
Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp F	Exposure, days	Corrosion Rate[a] mdd	Corrosion Rate[a] mpy	Remarks
0.06	15	D44	130	2	94.8	19.1	Very mild shallow pitting of high density plus low density pitting up to 0.4 mil deep.
		D45	130	2	76.1	15.4	
	150	D46	130	2	10.5	2.12	Very mild shallow pitting of low density.
		D47	130	2	16.9	3.41	
0.12	15	D11	160	2	38.4	7.76	General corrosion with patches of pitting (1mil deep).
		D12	160	2	52.7	10.7	
		D13	130	2	104.4	21.1	Mostly pitting corrosion of high density but small depth (0.4 mil).
		D14	130	2	103.7	21.0	
	150	D21	160	2	77.8	15.7	Mostly pitting corrosion of high density and small depth (0.4 mil)
		D22	160	2	86.9	17.6	
		D23	130	2	49.2	9.94	Mostly pitting corrosion of high density and moderate depth (0.7 mil).
		D24	130	2	63.7	12.9	
0.18	15	D25	130	2	73.5	14.8	Patches of light pitting corrosion (up to 0.5 mil deep).
		D26	130	2	92.4	18.7	
	150	D27	130	2	40.3	8.14	Patches of very light pitting corrosion (up to 0.5 mil deep).
		D28	130	2	31.6	6.38	

[a] mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

Table 15. Coupon-Weight-Loss Data for Die-Cast Zinc in 50 Weight Percent NTA-Based Detergents

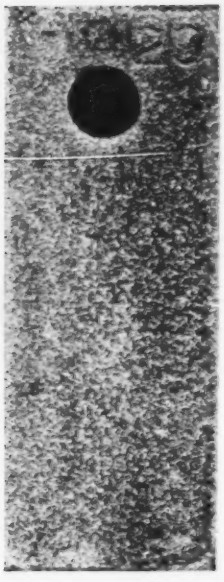
Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp F	Exposure, days	Corrosion Rate[a] mdd	Corrosion Rate[a] mpy	Remarks
0.06	15	D40	130	2	158	31.9	White voluminous deposit.
		D41	130	2	163	33.0	Uneven general corrosion.
	150	D42	130	2	22.9	4.6	Very low density pitting
		D43	130	2	17.6	3.6	corrosion up to 0.8 mil deep.
0.12	15	D9	160	2	234	44.3	White corrosion product.
		D10	160	2	222	44.8	General corrosion.
		D16	130	2	183	37.0	White corrosion product.
		D17	130	2	173	35.0	General Corrosion.
	150	D15	160	2	135	27.3	Mostly pitting corrosion of
		D18	160	2	115	23.2	low density and moderate width and depth (1.5 mil).
		D19	130	2	77.1	15.6	Slightly less pitting of
		D20	130	2	116	23.5	about same depth (1.5 mil). Small general corrosion.
0.18	15	D29	130	2	92.2	18.6	Mostly pitting corrosion of
		D30	130	2	115	23.2	medium density and low depth (up 0.5 mil).
	150	D31	130	2	154	31.0	General corrosion.
		D34	130	2	195.2	39.4	

[a] mdd = milligram/(decimenter)^2/day
mpy = mils penetration/year



P417

FIGURE 15. DIE-CAST ZINC COUPON D34 AFTER EXPOSURE
Note continuous deposit associated with general corrosion



P418

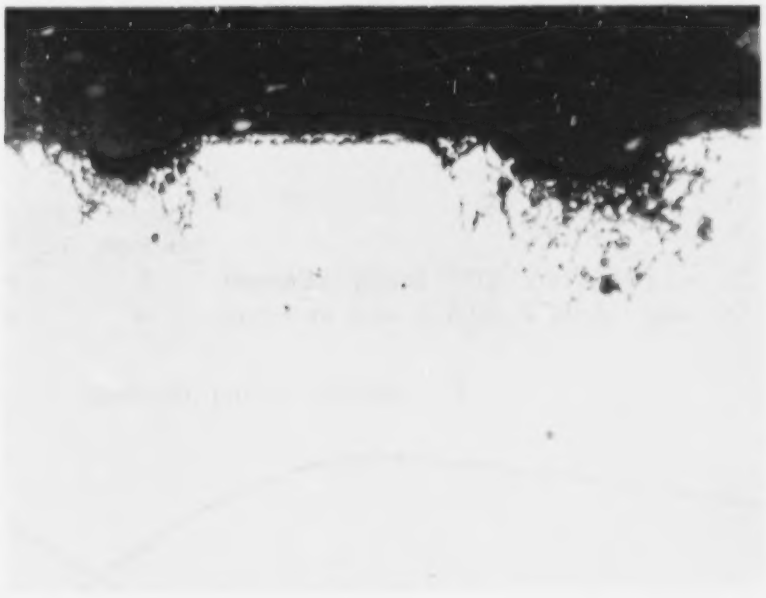
FIGURE 16. DIE-CAST ZINC COUPON D29 AFTER EXPOSURE
Note the moderate density and reasonably large size of pitting corrosion deposit.

P636

FIGURE 17. DIE-CAST ZINC COUPON D45 AFTER EXPOSURE
Note the very high density but smaller size of pitting corrosion deposits.

P638

FIGURE 18. DIE-CAST ZINC COUPON D43 AFTER EXPOSURE
Note the extremely low density of pitting corrosion deposits and low general corrosion.



C-3922 250X

FIGURE 19. CROSS SECTION OF PITTED AREA IN COUPON D18
Note extended fine corrosion paths beneath main pits.

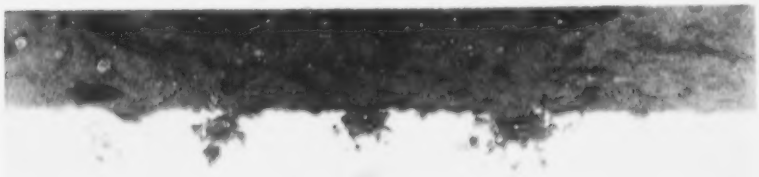


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FIGURE 20. CROSS SECTION OF PITTED AREA IN COUPON D14
Note smaller pit size than in Figure 18.

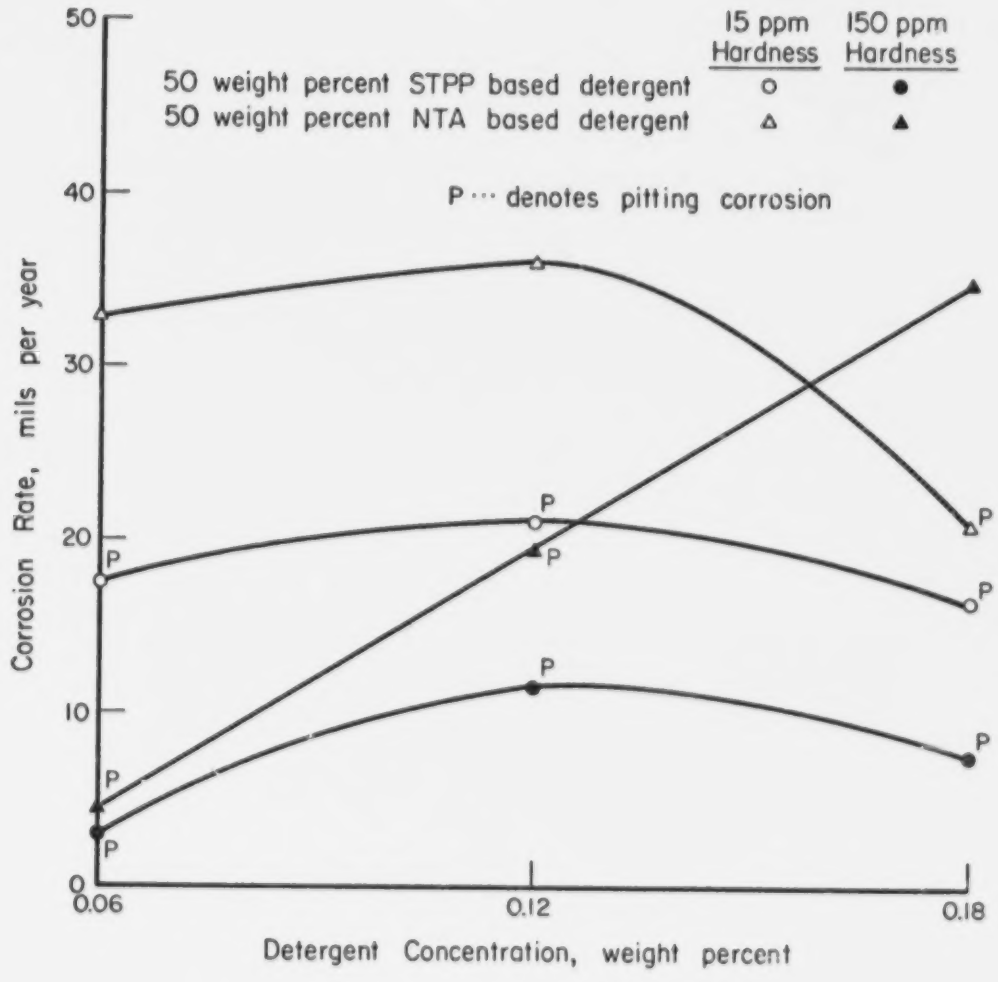


FIGURE 21. CORROSION RATE OF DIE-CAST ZINC AS A FUNCTION OF DETERGENT CONCENTRATION IN 15 PPM AND 150 PPM WATER HARDNESS AT 130 F

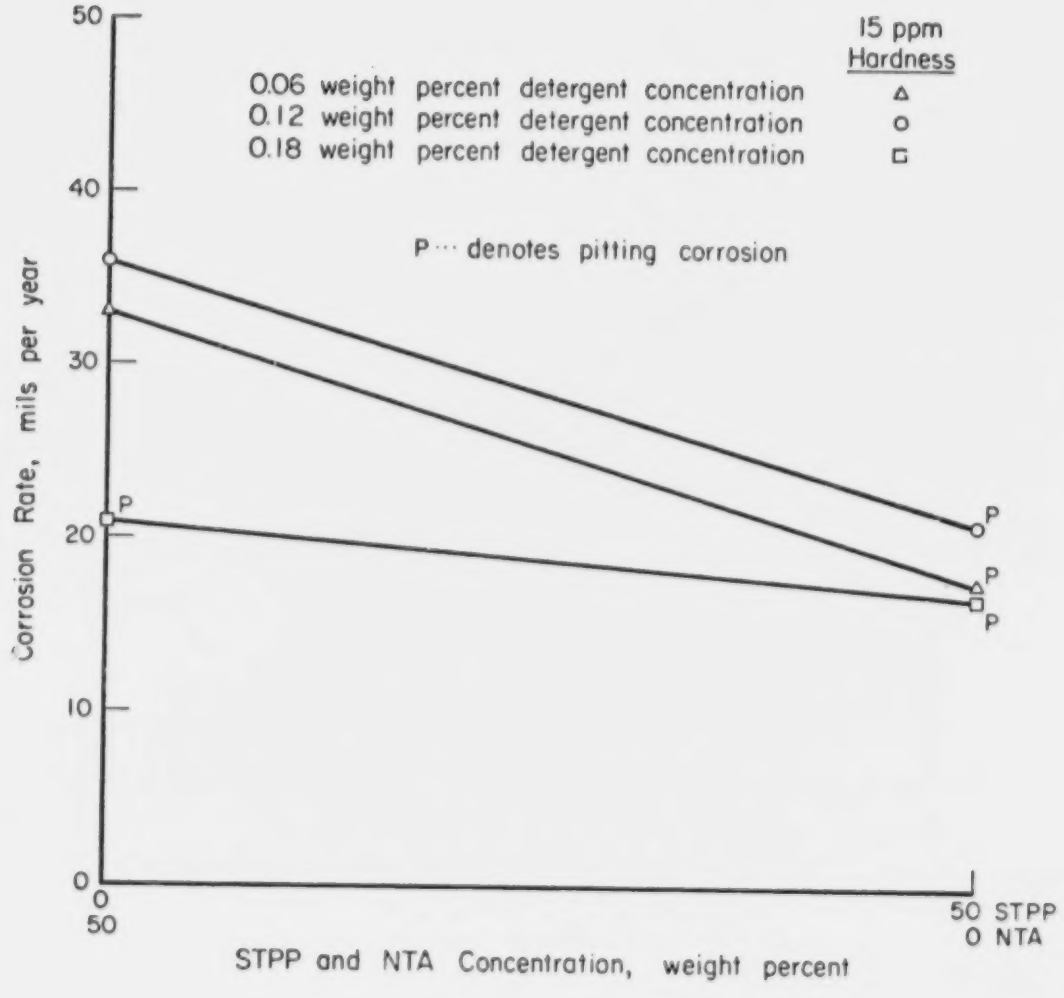


FIGURE 22 (a). CORROSION RATE OF DIE-CAST ZINC AS A FUNCTION OF STPP AND NTA CONCENTRATION AT 15 PPM WATER HARDNESS AND 130 F

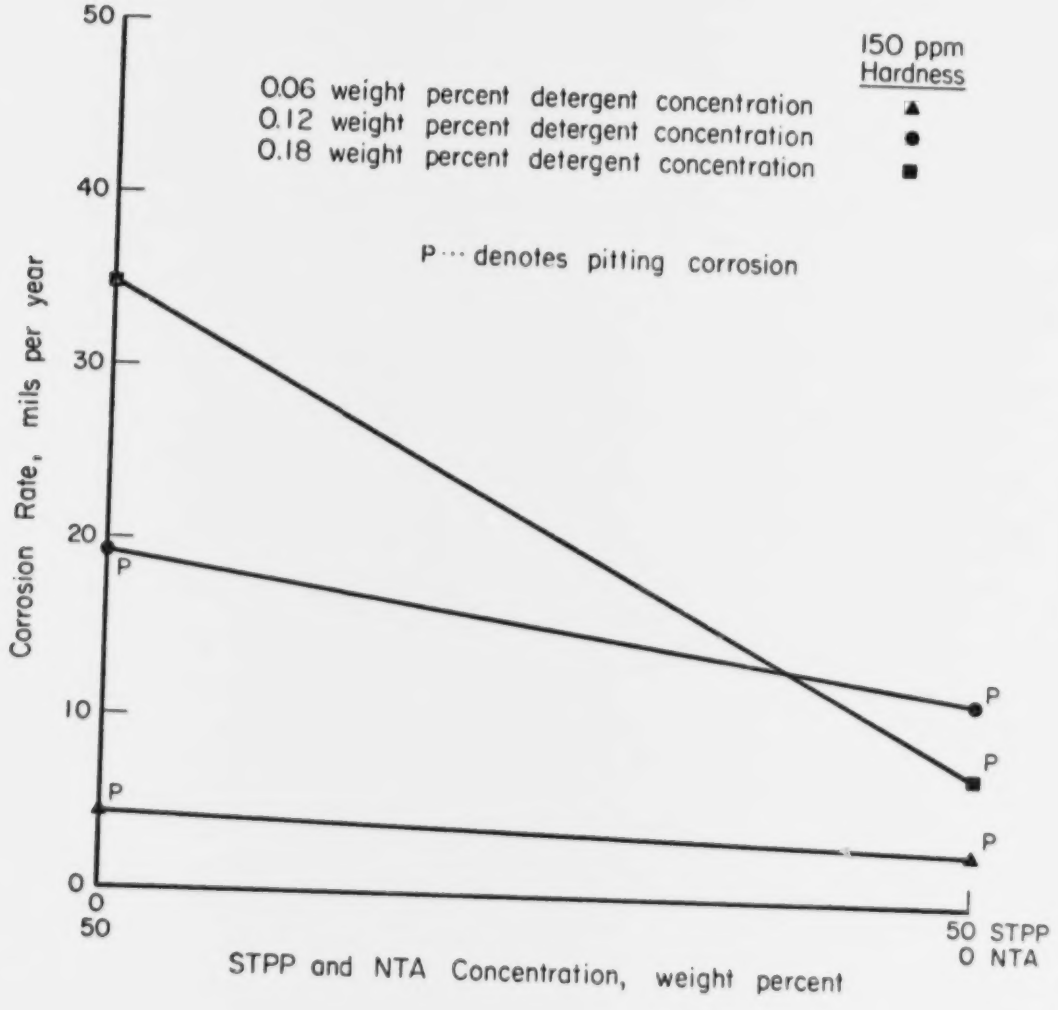


FIGURE 22(b). CORROSION RATE OF DIE-CAST ZINC AS A FUNCTION OF STPP AND NTA CONCENTRATION AT 150 PPM WATER HARDNESS AND 130 F

Figures 22(a) and 22(b) present the weight-loss data to indicate the increased corrosivity of NTA-based solutions over corresponding STPP-based solutions. As shown in Table 16, the corrosivity factor varied between 1.5 and 4.7.

Table 16. Increased Corrosivity Factors for NTA Solutions Over STPP Solutions with Die-Cast Zinc

Detergent Concentration, weight percent	15-ppm Hardness	150-ppm Hardness
0.06	1.9	1.5
0.12	1.7	1.7
0.18	1.3	4.7

In soft-water solutions, the corrosivity factor increased from 1.3 to 1.9 with decrease of concentration. However, in hard-water solutions, the corrosivity factor increased with increase of concentration to a maximum of 4.7.

A limited number of X-ray diffraction studies conducted on corrosion products indicate that $ZnSO_4$, $Zn(OH)_2$, and ZnO were the major components of these products. From coupons D25/D26 in an STPP-based solution, the compounds $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$, and ZnO were identified. Similar compounds $ZnSO_4 \cdot 6Zn(OH)_2 \cdot 4H_2O$, and ZnO were identified on coupons D31/D34 from an NTA-based solution.

The electrochemical linear polarization corrosion rates for die-cast zinc are summarized in Figure 23. These results were calculated using Equation 5 with values of $b_A = 0.070$ volt and $b_C = \infty$ determined from polarization curves. As seen from Figure 23, determined corrosion rates generally decreased from early values of about 15 mils per year to steady values after 1 to 3 days of 1 to 5 mils per year. It was apparent that the mixed solutions of 37.5 STPP-12.5 SNTA showed no marked differences in corrosion behavior from those of the pure STPP or SNTA solutions. It was evident that the linear polarization method gave corrosion rates of the order of 6 times smaller than rates determined by weight loss. As for 1100 Aluminum, brass, and copper, the data indicated that the presence of a poorly conducting film on die-cast zinc in these detergent solutions interferred with the evaluation of corrosion rate by this method. In many measurements with die-cast zinc, the measurements were similar to those in Figure 4(a); i.e., an unsymmetrical current response, indicating localized corrosion. This localized corrosion was evidenced as pitting of the electrodes.

201 Nickel

This metal was exposed to 0.12 weight solutions of both STPP- and NTA-based detergents with 15- and 150-ppm water hardness at 130 F for periods of 14 days. No weight loss was obtained on coupons, thus indicating corrosion rates of the order of 0.01 mil per year or less.

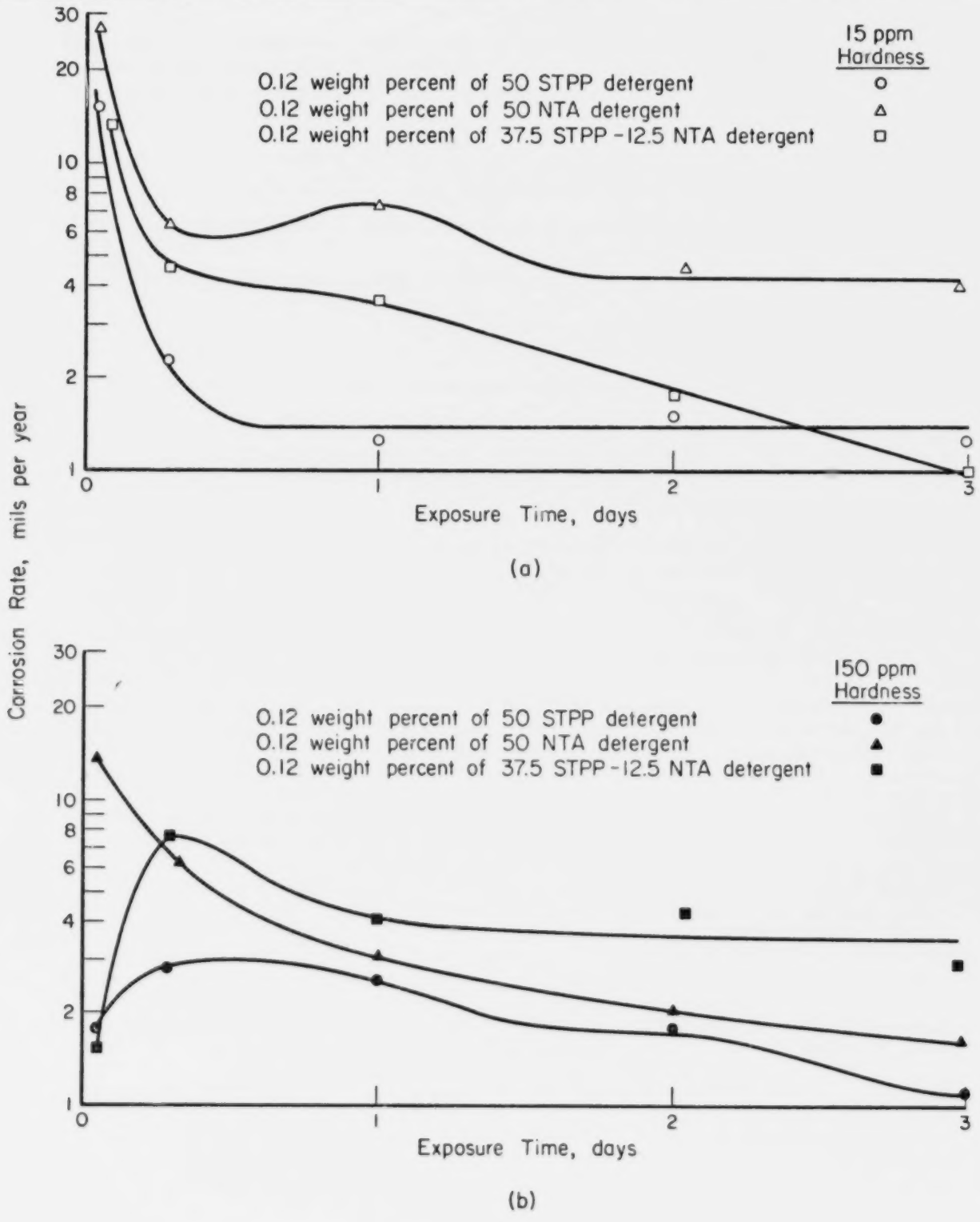

15 ppm Hardness
0.12 weight percent of 50 STPP detergent
0.12 weight percent of 50 NTA detergent
0.12 weight percent of 37.5 STPP - 12.5 NTA detergent
Corrosion Rate, mils per year
Exposure Time, days
(a)
150 ppm Hardness
0.12 weight percent of 50 STPP detergent
0.12 weight percent of 50 NTA detergent
0.12 weight percent of 37.5 STPP - 12.5 NTA detergent
Exposure Time, days
(b)

FIGURE 23. CORROSION RATE OF DIE-CAST ZINC AS A FUNCTION OF EXPOSURE TIME IN (a) 15 PPM AND (b) 150 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

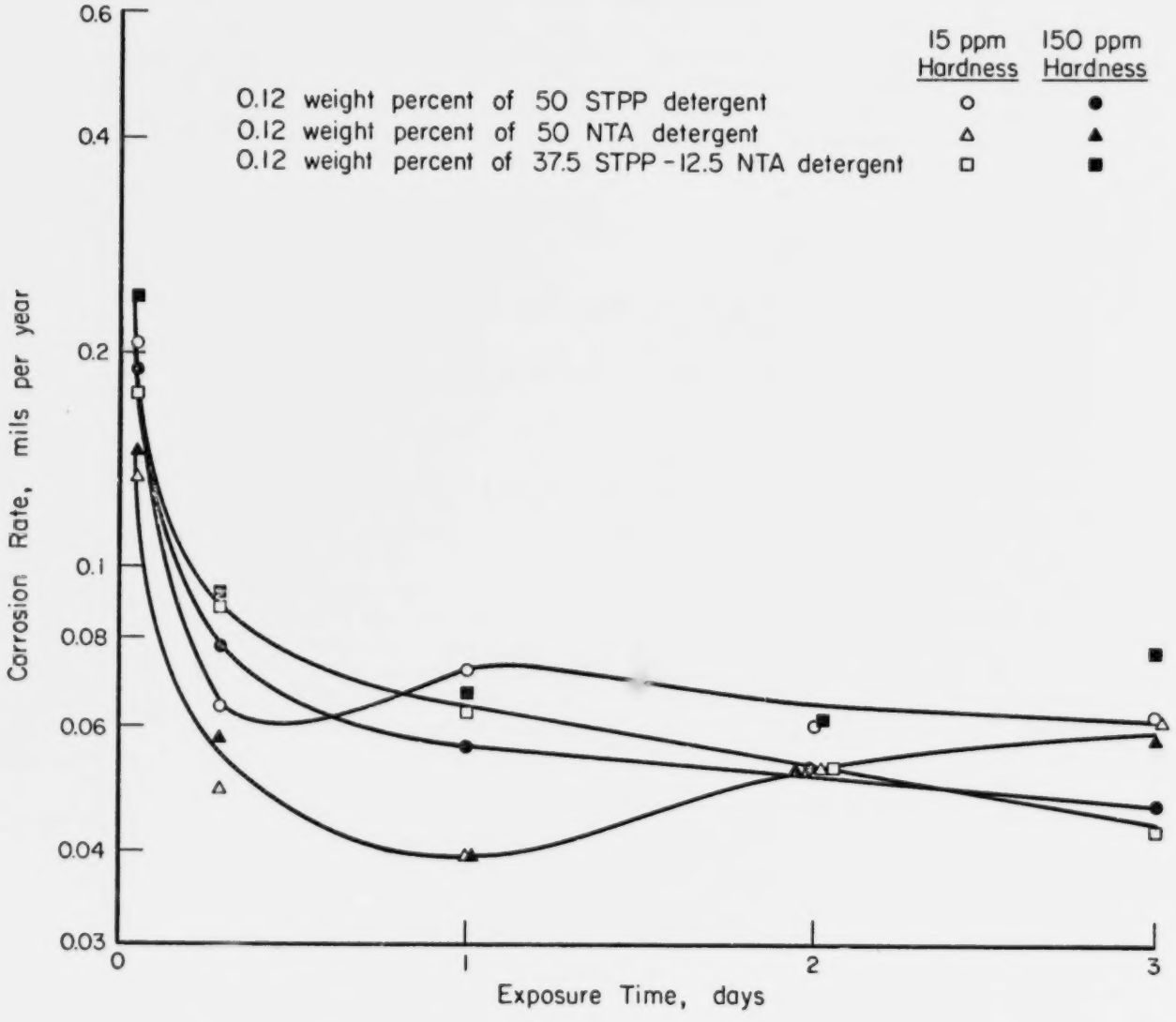


FIGURE 24. CORROSION RATE OF 201 NICKEL AS A FUNCTION OF EXPOSURE TIME AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

The electrochemical linear polarization measurements on this material are summarized in Figure 24. These results indicated for 0.12 weight solutions at 130 F that corrosion rates decreased appreciably from 0.2 to between 0.06 and 0.07 mil per year within a day's exposure. The decrease in corrosion rate paralleled a change in corrosion potential from about -0.27 to -0.21 volt versus SCE. It was evident that there was no marked difference in corrosion behavior in mixed solutions containing 37.5 STPP-12.5 NTA and the pure STPP and NTA-based solutions. Corrosion rates were not significantly different to indicate any marked differences in the corrosivity of the solutions. The corrosion rates of 0.06 to 0.07 mil per year indicated a very corrosion-resistant material that could be used safely in either the STPP- or NTA-based detergents.

Type 304 Stainless Steel

This metal was exposed to 0.12 weight percent solutions of both STPP and NTA-based detergents containing 15- and 150-ppm hardness at 130 F for periods of 14 days. As for 201 Nickel, this metal showed no weight loss, thus corrosion rates of the order of 0.1 mil per year or less were indicated.

The linear polarization corrosion rate measurements for this metal are summarized in Figure 25. The data in Figure 25 showed that initial corrosion rates of about 0.15 mil per year decreased to between 0.02 and 0.06 mil per year after 1 day's exposure. The decrease in corrosion rate paralleled changes in corrosion potential from about -0.26 to -0.21 volt versus SCE. Analysis of the data in Figure 25 indicated that detergent solutions in hard-water conditions; i.e., with more Cl^- were more corrosive than those in soft-water conditions. It was evident that mixed solutions of 37.5 STPP-12.5 NTA showed no marked corrosion differences to pure STPP or NTA solutions. Type 304 stainless steel which was slightly more corrosion resistant than 201 Nickel was the most corrosion-resistant material as measured in this study.

Type 420 Stainless Steel

This alloy was similarly exposed to 0.12 weight percent solutions of both STPP and NTA-based detergents with 15- and 150-ppm water hardness at 130 F for periods of 14 days. No weight loss was observed for this metal, thus indicating corrosion rates of the order of 0.01 mil per year or less.

Figure 26 shows the linear polarization corrosion rates determined for this alloy. It was apparent from Figure 26 that some changes occurred in corrosion rates in NTA and STPP solution in the soft-water condition but that, generally, corrosion rates were small (values between 0.06 and 0.15 mil per year). As for Type 304 stainless steel, the hard water conditions were the slightly more corrosive solutions. The corrosion rates of this material were slightly higher than those for Type 304 stainless steel and 201 Nickel, but they are representative of a good corrosion-resistant material.

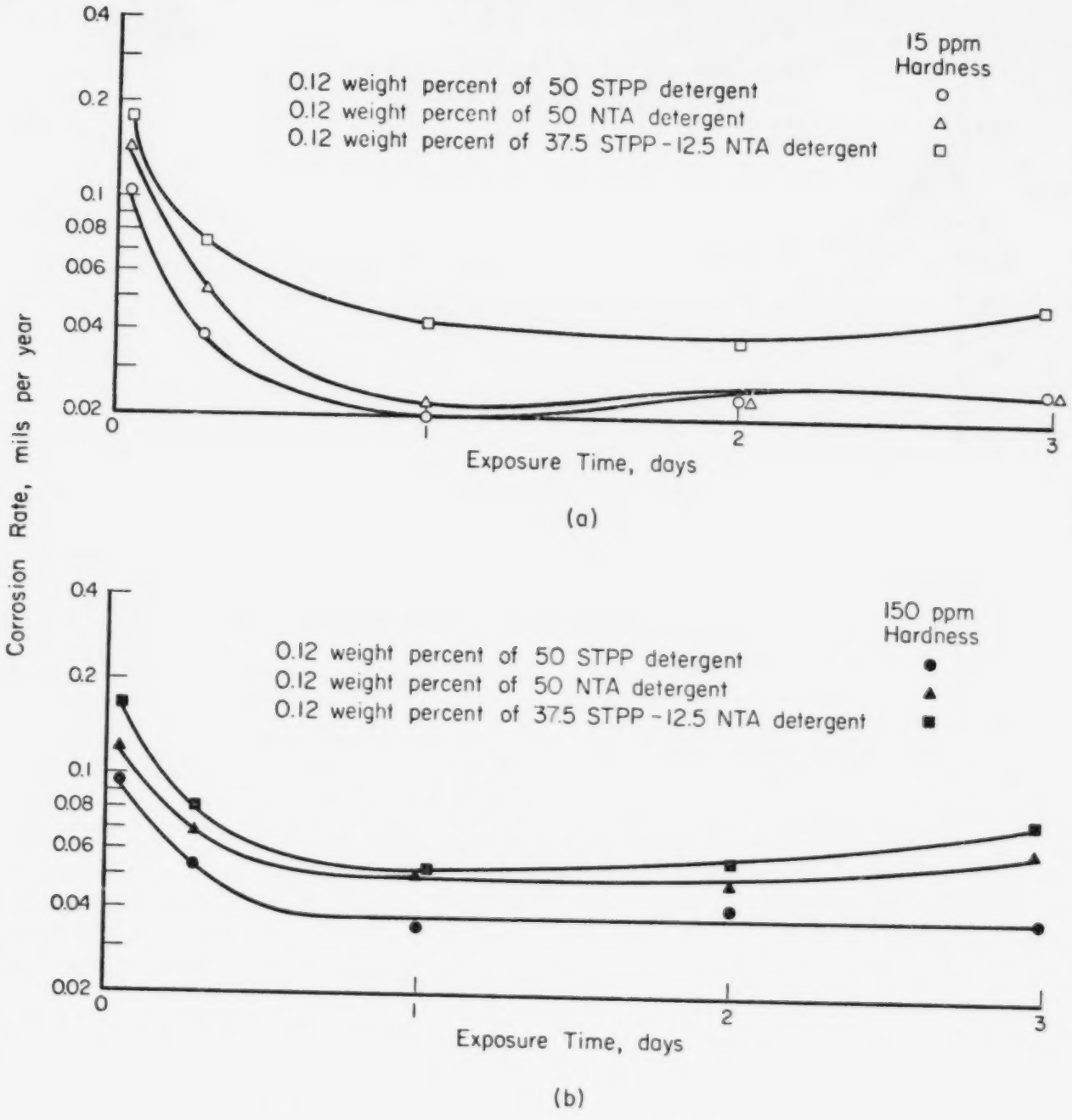


FIGURE 25. CORROSION RATE OF TYPE 304 STAINLESS STEEL AS A FUNCTION OF EXPOSURE TIME IN (a) 15 PPM AND (b) 150 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

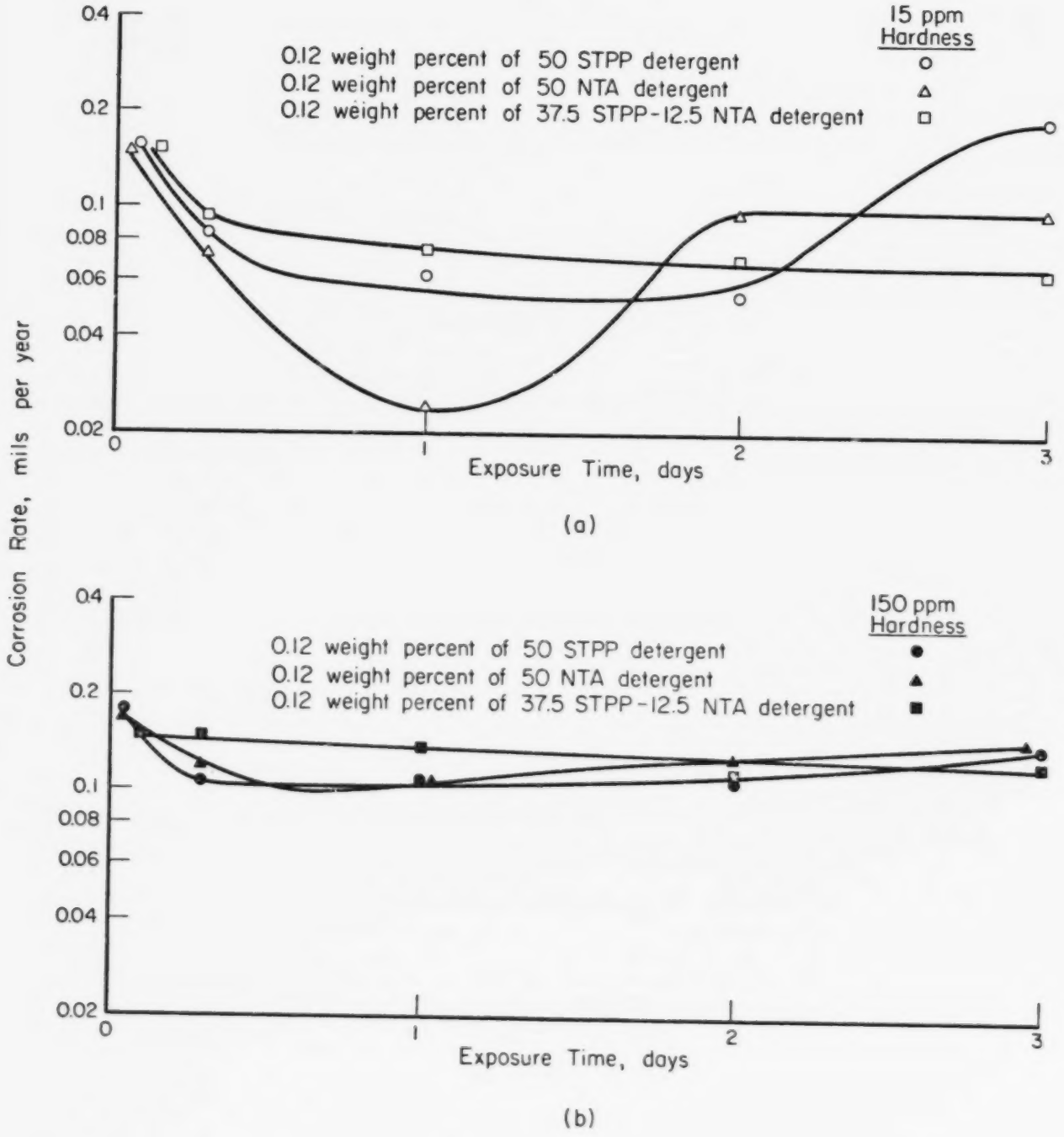


FIGURE 26. CORROSION RATE OF TYPE 420 STAINLESS STEEL AS A FUNCTION OF EXPOSURE TIME IN (a) 15 PPM AND (b) 150 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

1020 Carbon Steel

Weight loss data for 1020 carbon steel are summarized in Tables 17 and 18 for STPP and NTA solutions respectively. Weight losses for this material varied between 9.5 and 125 mg over the 2-day exposure periods to give corrosion rates between 4.4 and 57 mils per year. The corrosion rates varied, therefore, between low and very high. In general, four types of corrosion behavior were obtained as typified by Figures 27 to 30. Figure 27 shows the appearance of general, even corrosion; Figure 28 shows general corrosion with heavier localized corrosion. This material also evidenced localized etching corrosion which would occur with no evidence of an adherent deposit as shown by Figure 29 or under a reasonably adherent deposit as shown by Figure 30. The etched areas generally revealed a faceted structure in surface microscopy but metallography indicated that this corrosion did not penetrate beyond a surface layer, e.g., as grain-boundary corrosion.

The weight-loss data are summarized in Figure 31. Although trends are not evident in Figure 31 (due to localized corrosion producing misleading low overall corrosion rates), this materials action is probably similar to the others. Thus, considering that the localized corrosion results represented by 'L' in Figure 31 are probably much higher rates, it appears that the corrosion rates probably increase with increase in detergent concentration. The NTA-based solutions in the soft water condition appear to be the most corrosive of all. It does appear also that an increase in detergent concentration favors localized corrosion for both STPP and NTA solutions.

The weight-loss data shown in Figures 32(a) and 32(b) allow determination of the increased corrosivity factor for NTA solutions over STPP solutions. These results summarized in Table 19, show that the increased corrosivity

Table 19. Increased Corrosivity Factors for NTA Solutions Over STPP Solutions with 1020 Carbon Steel

Detergent Concentration, weight percent	15-ppm Hardness	150-ppm Hardness
0.06	2.9	4.2
0.12	7.1	1.0
0.18	-3.0[a]	2.6

[a] STPP solution more corrosive than NTA solution.

factor varied between 1.0 and 7.1 but that in 0.18 weight percent soft water solutions, the STPP was more corrosive. No marked trends with effect of concentration, as were evident for other metals, would indicate that the high corrosion rates under filming and nonfilming conditions disguised such correlations. It was apparent, however, that NTA solutions in hard water were consistently more corrosive.

The linear polarization measurements on 1020 carbon steel are summarized in Figure 33. These results suggest that, unlike results for other materials,

Table 17. Coupon-Weight-Loss Data for 1020 Carbon Steel in 50 Weight Percent STPP-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate(a) mdd	mpy	Remarks
0.06	15	H45	130	2	60.7	11.1	Dark brown deposit. General corrosion plus heavier localized corrosion.
		H46	130	2	56.0	10.2	
	150	H47	130	2	26.4	4.83	Bright appearance. General corrosion.
		H48	130	2	23.8	4.35	
0.12	15	H11	160	2	43.9	8.03	Local etching corrosion.
		H12	160	2	70.2	12.9	
		H13	130	2	41.4	7.58	Local etching corrosion.
		H14	130	2	40.1	7.34	
	150	H21	160	2	167.9	30.7	Mostly heavy general etching plus some localized.
		H22	160	2	213.3	39.0	
		H23	130	2	109.5	20.0	Mostly general mild etching.
		H24	130	2	138.3	25.3	
0.18	15	H25	130	2	273.8	50.1	General even corrosion
		H26	130	2	271.6	49.7	
	150	H27	130	2	68.8	12.6	Local etching corrosion.
		H28	130	2	58.0	10.6	

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

Table 18. Coupon-Weight-Loss Data for 1020 Carbon Steel in 50 Weight Percent NTA-Based Detergents

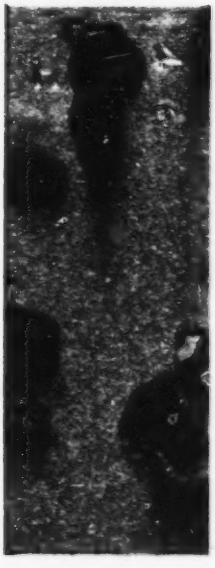
Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate[(a)] mdd	mpy	Remarks
0.06	15	H41	130	2	161	29.5	General and some heavier localized corrosion.
		H42	130	2	157	28.7	
	150	H43	130	2	116	21.2	Reddish-brown film. Even general corrosion.
		H44	130	2	85.8	15.7	
0.12	15	H9	160	2	152	27.8	Localized shallow etching (2-mil deep) under corrosion product.
		H10	160	2	140	25.6	
		H18	130	2	277	50.6	General corrosion.
		H19	130	2	311	56.9	
	150	H15	160	2	180	32.9	Intense local etching corrosion.
		H16	160	2	207	37.8	
		H17	130	2	130.1	23.8	Local etching corrosion.
		H20	130	2	110.0	20.1	
0.18	15	H29	130	2	97.9	17.9	Local etching corrosion.
		H30	130	2	81.6	14.9	
	150	H31	130	2	185	33.9	Localized and general corrosion.
		H32	130	2	137	25.1	

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

P416
FIGURE 27. 1020 CARBON STEEL COUPON H26 AFTER EXPOSURE
Note general corrosion.

P639
FIGURE 28. 1020 CARBON STEEL COUPON H41 AFTER EXPOSURE
Note general corrosion and heavier localized corrosion.

P419
FIGURE 29. 1020 CARBON STEEL COUPON H27 AFTER EXPOSURE
Note corrosion-deposit-free localized corrosion.



P638
FIGURE 30. 1020 CARBON STEEL COUPON H46 AFTER EXPOSURE
Note corrosion-deposit-covered localized corrosion.

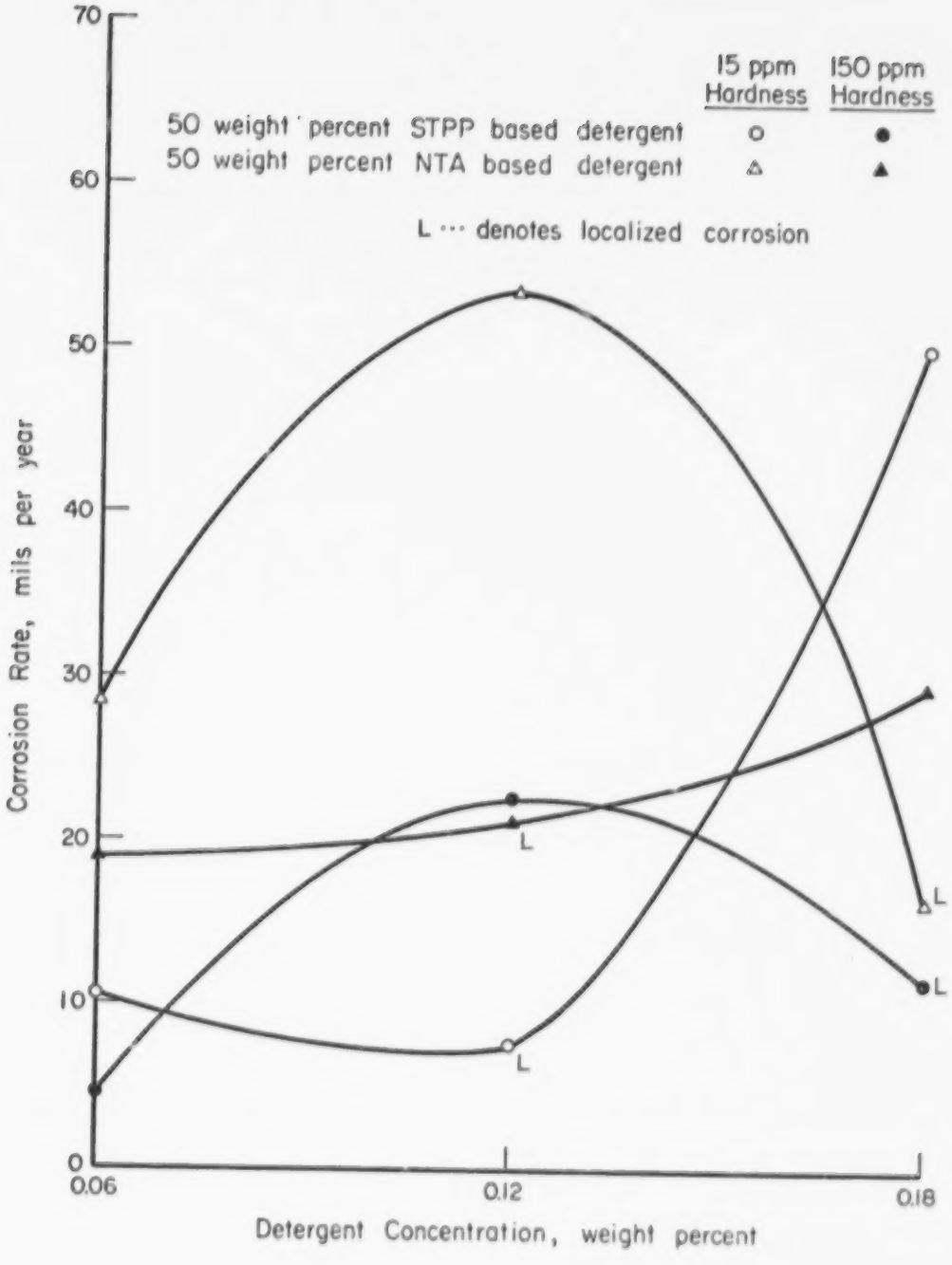


FIGURE 31. CORROSION RATE OF 1020 CARBON STEEL AS A FUNCTION OF DETERGENT CONCENTRATION IN 15 PPM AND 150 PPM WATER HARDNESS AT 130 F

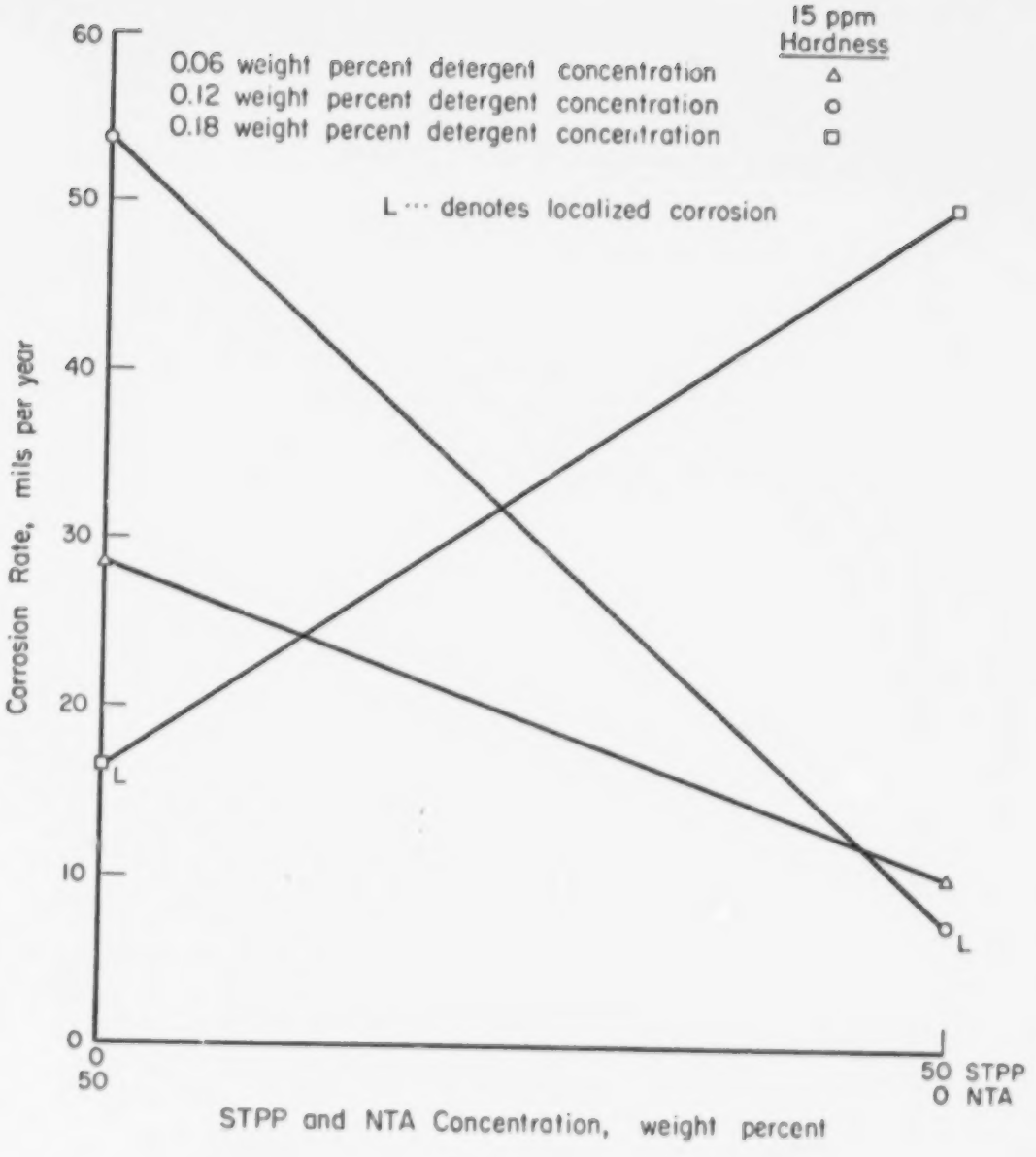


FIGURE 32 (a). CORROSION RATE OF 1020 CARBON STEEL AS A FUNCTION OF STPP AND NTA CONCENTRATION AT 15 PPM WATER HARDNESS AND 130 F

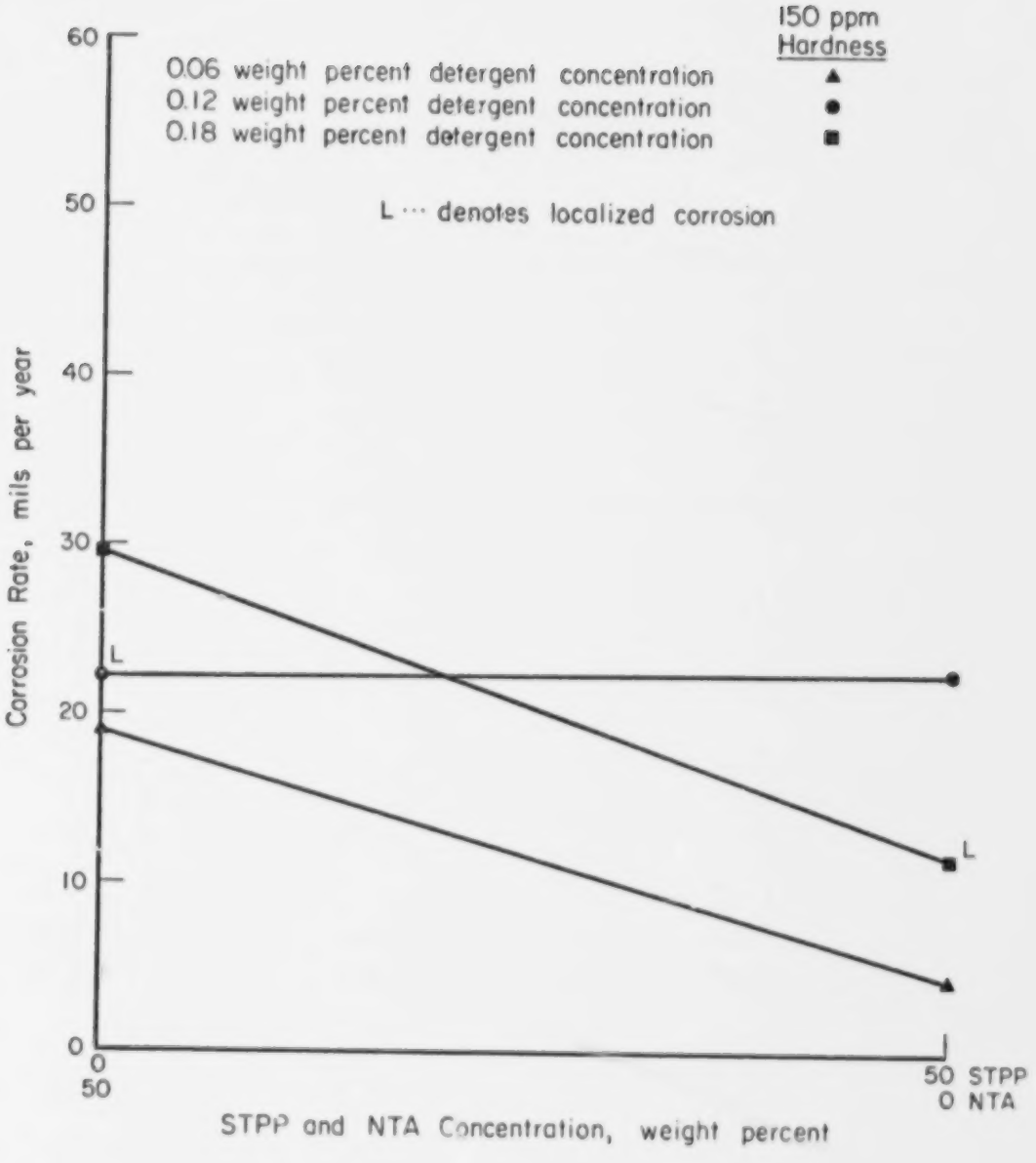


FIGURE 32 (b). CORROSION RATE OF 1020 CARBON STEEL AS A FUNCTION OF STPP AND NTA CONCENTRATION AT 150 PPM WATER HARDNESS AND 130 F

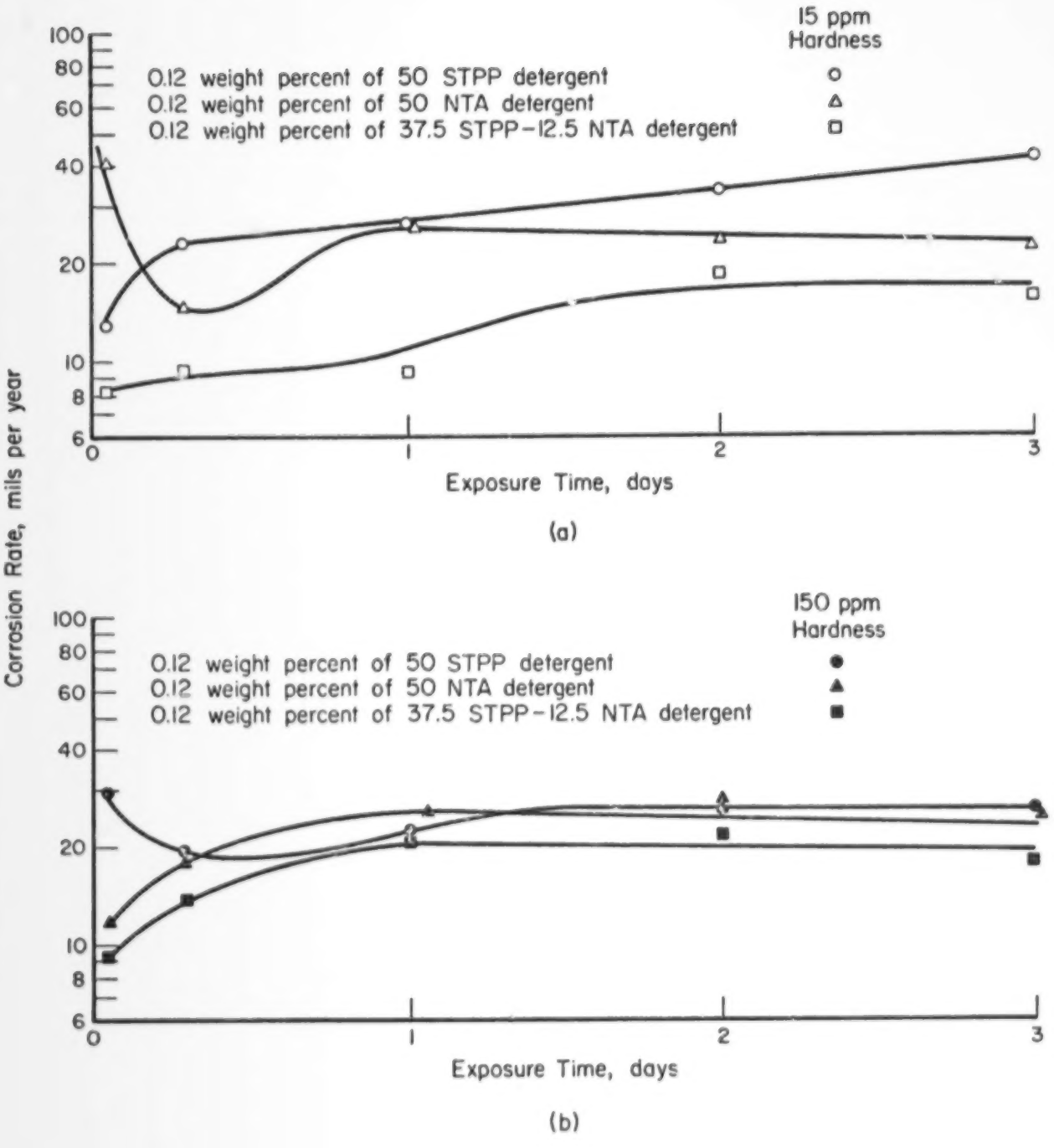


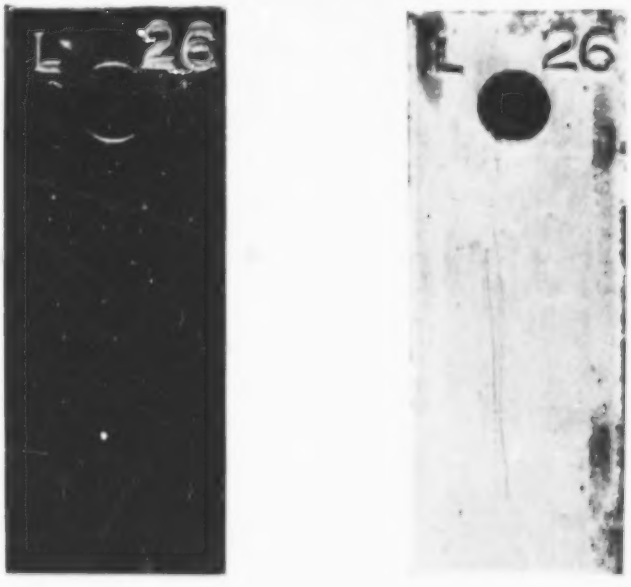
FIGURE 33. CORROSION RATE OF 1020 CARBON STEEL AS A FUNCTION OF EXPOSURE TIME IN (a) 15 PPM AND (b) 150 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

the corrosion rate increased over the first day's exposure to steady state. This behavior paralleled a change in corrosion potential from about -0.6 to -0.8 volt versus SCE. The linear polarization results which were evaluated using the determined values of b_A = 0.14 volt and b_C = ∞ and Equation 5 gave corrosion rates between about 15 and 40 mils per year which were in good agreement with weight loss data. The linear polarization results appeared to indicate that STPP solutions were more corrosive than NTA solutions with the mixed STPP-NTA solutions of intermediate behavior. The STPP solution in the soft-water condition appeared to be the most corrosive. In several solutions, the linear polarization method gave responses similar to that shown in Figure 4(a) indicating a localized form of corrosion, as evidenced on the electrode after experiments.

A limited number of studies were made of corrosion products by X-ray diffraction. Coupons H27/H28 and H45/H46 from STPP solutions were found to contain a $Fe(OH)_3$ product as did coupons H29/H30 from an NTA solutions. Coupons H43/H44 also from a NTA solution showed the presence of a δ -FeOOH product with a faint pattern for $NaFeO_2$ and a very faint pattern for Fe_3O_4. It appears that $Fe(OH)_3$ which was sharper from samples off coupons H45/H46 was aided by the soft-water condition of the low-STPP concentration. This solution corresponded to the lowest pH value of 10.0 of these solutions producing this corrosion product.

Chemical Lead

Tables 20 and 21 summarize the weight-loss data for chemical lead in STPP and NTA solutions, respectively. Weight losses varied between 11 and 223 mg per coupon over the 5-day exposure periods. Corrosion rates between 1.3 and 29 mils per year were moderately low and very high, respectively. The corrosion of the material appeared to be general and a dull white or gray deposit typified in Figure 34 was observed on the specimens.



P415 (a) (b)

FIGURE 34. CHEMICAL LEAD COUPON L26 (a) BEFORE AND (b) AFTER EXPOSURE. Note fine white deposit.

Table 20. Coupon-Weight-Loss Data for Chemical Lead in 50 Weight Percent STPP-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate(a) mmd	Corrosion Rate(a) mpy	Remarks
0.06	15	L45	130	5	34.4	4.37	Dull greenish-gray film. General corrosion.
		L46	130	5	32.8	4.17	
	150	L47	130	5	10.1	1.28	Dull light gray film. General corrosion.
		L48	130	5	13.4	1.70	
0.12	15	L11	160	5	25.1	3.19	Dull gray. General corrosion.
		L12	160	5	25.4	3.23	
		L13	130	5	54.3	6.90	Dull gray with yellow spotted areas. General corrosion.
		L14	130	5	62.3	7.91	
	150	L21	160	5	72.1	9.16	Dull gray and traces of white and brown deposits. General corrosion.
		L22	160	5	78.9	10.0	
		L23	130	5	65.3	8.29	Dull gray with traces of white deposit. General corrosion.
		L24	130	5	57.3	7.28	
0.18	15	L25	130	5	177.2	22.5	Fine dull white deposit. General corrosion.
		L26	130	5	150.8	19.2	
		L27	130	5	95.0	12.1	Dull gray with trace of white. General corrosion.
		L28	130	5	100.2	12.7	

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

Table 21. Coupon-Weight-Loss Data for Chemical Lead in 50 Weight Percent NTA-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate[a] mdd	Corrosion Rate[a] mpy	Remarks
0.06	15	L41	130	5	104	13.2	Fine white deposit. General corrosion.
		L42	130	5	119	15.2	
	150	L43	130	5	43.8	5.56	Dull light gray film. General corrosion.
		L44	130	5	28.3	3.59	
0.12	15	L9	160	5	219	27.8	Fine crystalline deposit. General corrosion.
		L10	160	5	226	28.7	
		L16	130	5	112	14.2	Fine crystalline deposit. General corrosion.
		L17	130	5	137	17.4	
	150	L15	160	5	169	21.4	Coarse crystalline white deposit. General corrosion.
		L18	160	5	155	19.7	
		L19	130	5	109	13.8	White crystalline deposit. General corrosion.
		L20	130	5	101	12.8	
0.18	15	L29	130	5	146	18.5	Fine white deposit. General corrosion.
		L30	130	5	174	22.0	
	150	L31	130	5	131	16.6	Dull gray with traces of yellowish-green white deposit. General corrosion.
		L32	130	5	127	16.1	

(a) mdd = milligram/(decimeter)^2/day
mpy = mils penetration/year

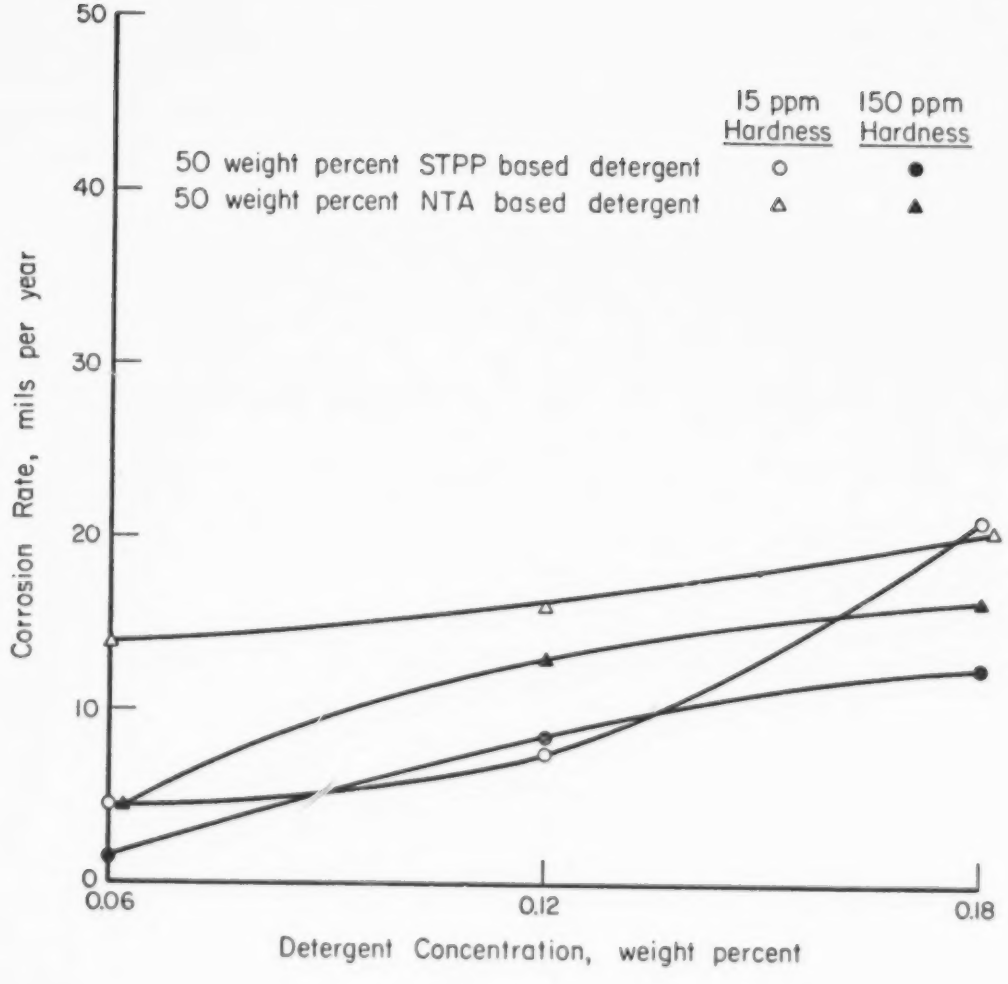


FIGURE 35. CORROSION RATE OF CHEMICAL LEAD AS A FUNCTION OF DETERGENT CONCENTRATION IN 15 PPM AND 150 PPM WATER HARDNESS AT 130 F

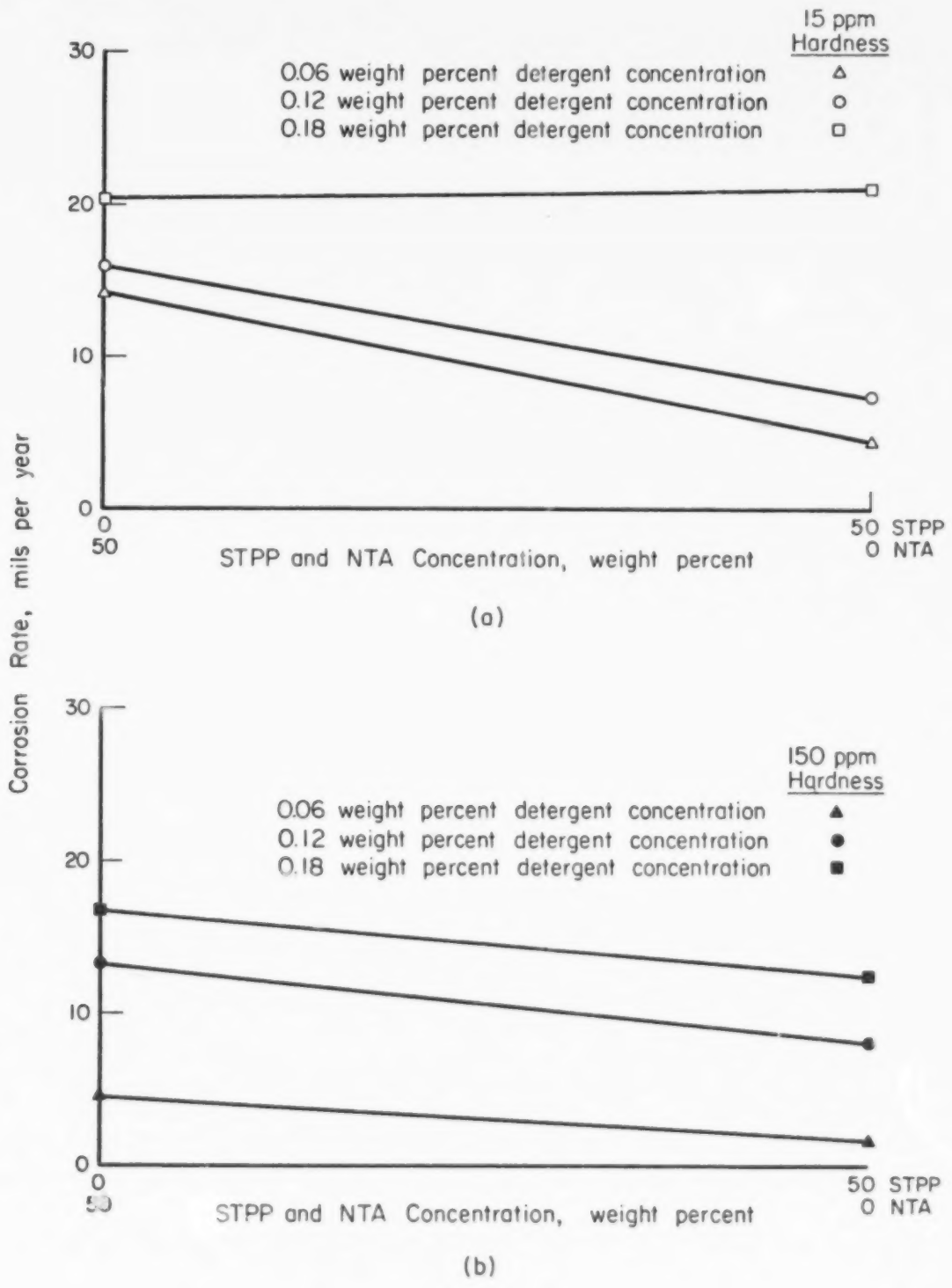


FIGURE 36. CORROSION RATE OF CHEMICAL LEAD AS A FUNCTION OF STPP AND NTA CONCENTRATION AT (a) 15 PPM AND (b) 150 PPM WATER HARDNESS AND 130 F

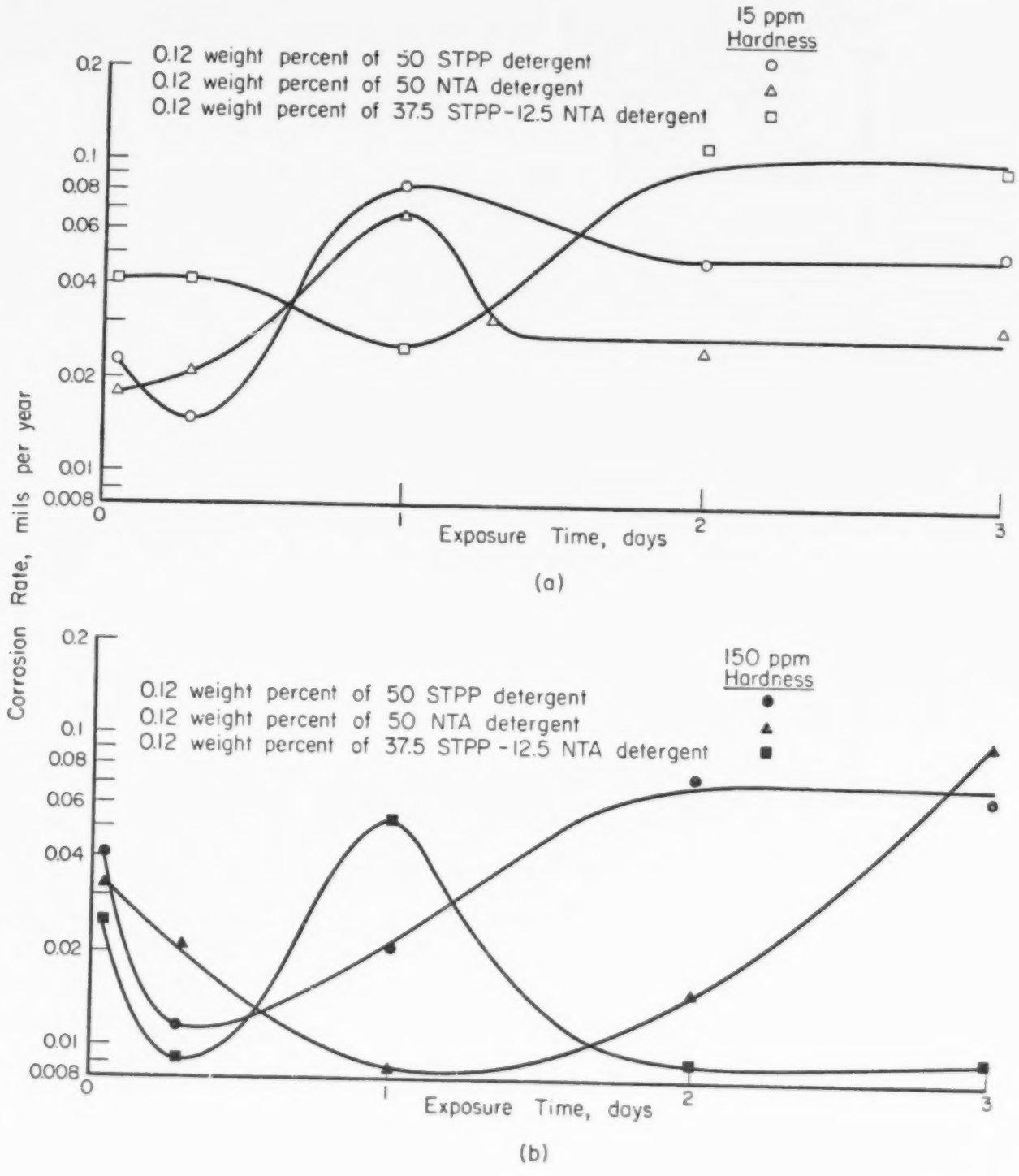


FIGURE 37. CORROSION RATE OF CHEMICAL LEAD AS A FUNCTION OF EXPOSURE TIME IN (a) 15 PPM AND (b) 150 PPM HARDNESS SOLUTIONS AT 130 F AND USE OF THE LINEAR POLARIZATION METHOD

Figure 35 summarizes the weight-loss data in Tables 20 and 21. The data indicated that the corrosion rate of chemical lead increased with increase of detergent concentration and that NTA solutions appeared to be more corrosive than the corresponding STPP solutions. The most corrosive solutions were those based upon NTA in the soft-water condition.

Figure 36 shows the weight-loss data from which the increased corrosivity of the NTA solutions could be determined. These results are summarized in Table 22 which shows that the corrosivity factor varied between 1.0 and 3.1. Values for both soft- and hard-water conditions are similar and increased with decreased detergent concentration.

Table 22. Increased Corrosivity Factors for NTA Solutions Over STPP Solution with Chemical Lead

Detergent Concentration, weight percent	15-ppm Hardness	150-ppm Hardness
0.06	3.1	3.0
0.12	2.1	1.6
0.18	1.0	1.3

The linear polarization measurements on chemical lead are summarized in Figure 37. As seen from Figure 37, large changes in corrosion rates were measured over the first-day exposure period. Generally the corrosion potentials varied between -0.5 and -0.6 volt versus SCE but did not parallel the marked changes in corrosion rate. The corrosion rates were calculated using Equation 5 and the determined values of b_A = 0.30 volt and $b_C = \infty$ from polarization curves. It was apparent that the corrosion rates measured by the linear polarization method were very much smaller than those determined by weight loss. Again, it would appear that poorly conducting films produced on the material in these solutions gave a low assessment of corrosion rate.

X-ray diffraction identified corrosion products of $Pb_4O(PO_4)_2$, $Pb_5(PO_4)_3OH$ and Na_2SO_4 on coupons L25/L26 from a STPP solution. Coupons L29/L30 from a NTA solution indicated products of $Pb_3(CO_3)_2(OH)_2$ and PbO(red). The product PbO (red) was also identified on the coupons L31/L32 from another NTA solution. Lead was the only material in which phosphate deposits were identified on materials exposed to STPP-based detergents.

Cast-Iron Soil-Pipe Material

The weight-loss data for this material are shown in Tables 23 and 24 for as-prepared and soil STPP and NTA solutions respectively. Soil-pipe studies were conducted at 130 F since this temperature related to studies of other materials and was only slightly higher than the usual temperature (115 to 120 F) of detergent solutions going to drain. As shown in Table 23, weight-loss data on this material was obtained over exposure periods of 2 and 7 days. Two exposure periods were used because 2-day corrosion rates were very high and, therefore, there was a need to determine if these corrosion rates became stiffled on longer exposure. The corrosion rates of this material were always very high (16 to 120 mils per year) in the fresh detergent solutions (Table 23).

Table 23. Coupon-Weight-Loss Data for Cast Iron Soil Pipe in STPP and NTA-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate(a) mdd	Corrosion Rate(a) mpy	Remarks
0.12 of 50 wt. percent NTA-based detergent	15	M1	130	2	602	120	Mottled brown color. General corrosion.
		M2	130	2	595	119	
		M9	130	7	391	78.2	Light and dark brown. General corrosion.
		M10	130	7	416	83.1	
	150	M3	130	2	144	28.8	Mottled brown color. Mostly general corrosion with some pitting. (<0.5 mil depth).
		M4	130	2	150	30.0	
		M11	130	7	513	103	Light reddish-brown. General corrosion.
		M12	130	7	325	65.0	
0.12 of 50 wt. percent STPP-based Detergent	15	M5	130	2	80.9	16.2	Mottled brown color. Mostly general corrosion with trace of pitting (<0.5 mil depth).
		M6	130	2	100	20.0	
		M13	130	7	175	34.9	Light-brown and black deposit. Mostly general corrosion with a little localized.
		M14	130	7	267	53.3	
	150	M7	130	2	246	49.0	Localized and general corrosion.
		M8	130	2	180	35.9	
		M15	130	7	233	46.5	Encrusted brown, gray, and black deposit. Mostly general corrosion with more intense localized.
		M16	130	7	230	45.9	

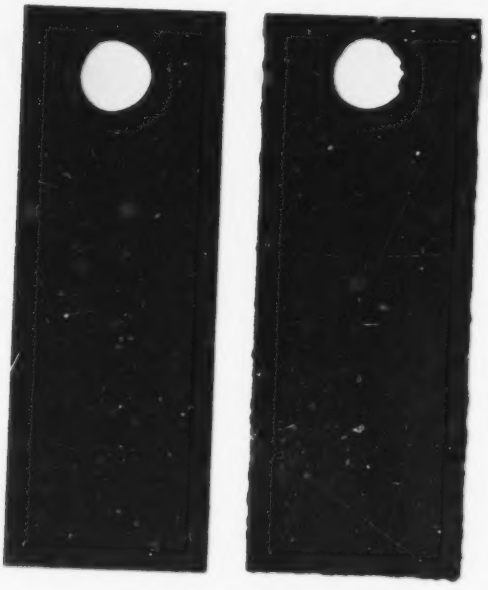
(a) mdd = milligran/(decimeter)^2/day.
mpy = mils penetration/year.

Table 24. Coupon-Weight-Loss Data for Cast Iron Soil Pipe in Soiled STPP and NTA-Based Detergents

Detergent Concentration, weight percent	Hardness, ppm	Coupon	Temp, F	Exposure, days	Corrosion Rate[a] mdd	Corrosion Rate[a] mpy	Remarks
0.12 of 50 wt. percent NTA-based detergent	15	M17	130	2	383	76.6	Light and reddish-brown. Localized corrosion up to 0.4 mil deep and pits up to 0.2 mil deep.
		M18	130	2	354	70.8	
	150	M19	130	2	227	45.4	Light brown non-adherent deposit. Large areas of localized corrosion.
		M20	130	2	147	29.4	
0.12 of 50 wt. percent STPP-based detergent	15	M21	130	2	175	35.1	Yellow and light brown deposit. Localized corrosion up to 0.4 mil deep and pits up to 0.2 mil deep.
		M22	130	2	280	56.0	
	150	M23	130	2	74.8	15.0	Pale yellow, poorly adherent deposit. Mild general corrosion.
		M24	130	2	45.2	9.0	

(a) mdd = milligram/(decimeter)^2/day.
mpy = mils penetration/year.

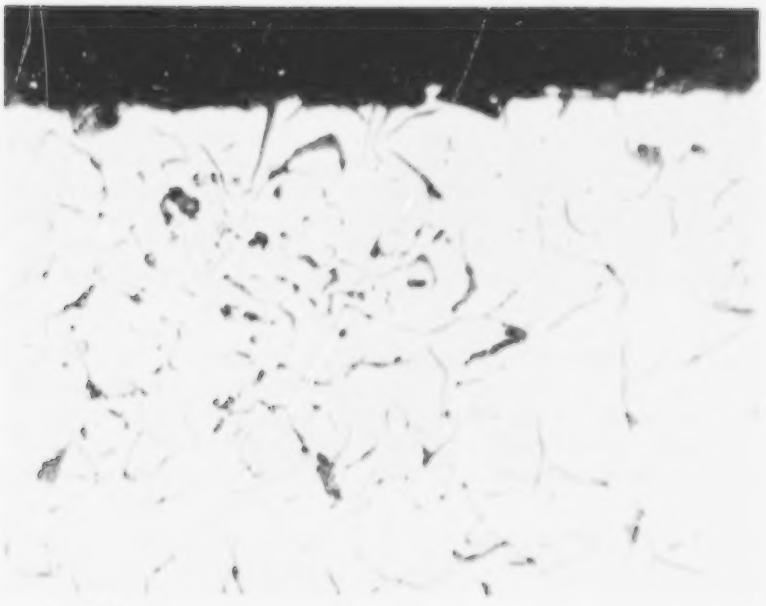
In the 2-day exposure period, the soft-water condition was more corrosive in NTA solutions at 120 mils per year than STPP solutions with a rate of about 18 mils per year. In the hard-water condition, however, the STPP solution was slightly more corrosive at 43 mils per year compared to 30 mils per year with NTA solution. Figure 38(a) shows the typical appearance of coupons M1/M2, M3/M4, M5/M6, and Figure 38(b), the appearance of coupons M7/M8 in this series.



P425 (a) (b)

FIGURE 38. CAST-IRON COUPONS (a) M4 and (b) M8 AFTER EXPOSURE. Note general corrosion of M4 and mixed corrosion of M8.

From the data in Table 23, it was apparent that the 7-day exposure in NTA solutions showed a decrease from 120 to 81 mils per year in soft-water solution and an increase from 30 to 84 mils per year in hard-water solutions. It appeared that, in 7 days, corrosion rates of 81 to 84 mils per year obtained were independent of water hardness. The decrease in corrosion rate from 120 to 81 mils per year in the soft-water solutions was undoubtedly due to the formation of a graphitized layer as shown by comparison of Figures 39 and 40. The formation of a thin graphitized layer was also noted on coupons M13/M14 in the STPP solution.



C-3924 250X

FIGURE 39. CROSS SECTION OF COUPON M1

Note general, even corrosion and only thin graphitized layer.

C-3925 250X

FIGURE 40. CROSS SECTION OF COUPON M10

Note the thick graphitized layer.

In STPP solutions, the 7-day exposure indicated an increase of corrosion rate from 18 to 44 mils per year in soft-water solutions and from 43 to 46 mils per year in hard-water solutions. Thus, as for NTA solutions, the 7-day exposure period gave corrosion rates that were independent of water hardness. The rates of 44 to 46 mils per year in the STPP solutions were much lower, however, than the rates of 81 to 84 mils per year in the NTA solutions. The independence of corrosion rate with water hardness was probably due to controlled dissolution through surface films which more readily occurred in NTA solutions. X-ray diffraction of the deposit from coupons M7/M8, however, failed to show the presence of crystalline corrosion products.

The weight-loss data in Table 23 is summarized in Figure 41 to allow evaluation of the increased corrosivity factors of NTA solutions over corresponding STPP solutions. These factors are summarized in Table 25. The data in Table 25 indicated, with the exception of the hard-water condition and 2-day exposure period, the NTA solutions were more corrosive

Table 25. Increased Corrosivity Factors for NTA Solutions Over STPP Solutions With Cast Iron

Detergent Concentration, weight percent	Exposure, days	15-ppm Hardness	150-ppm Hardness
0.12	2	6.7	-1.4(a)
0.12	7	1.8	1.8

(a) STPP solution more corrosive than NTA solution

than corresponding STPP solutions with increased corrosivity factors between 1.8 and 6.7. It appeared that, with the occurrence of graphitized layers within the 7-day exposure period, the corrosivity factor became equal in both hard-water and soft-water solutions at a value of 1.8.

A number of coupons have been exposed to STPP and NTA solutions which have been deliberately contaminated in order to simulate spent or soiled solutions which go to the drain. These solutions were made up using metal-salt additions of $Fe_2(SO_4)_3 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $PbSO_4$, and $Al_2(SO_4)_3 18H_2O$ to 0.12 weight percent detergent solutions in proportion to the predetermined corrosion rates of the corresponding metals in these solutions. These data are summarized in Table 26. The soft-water and hard-water NTA solutions were adjusted to pH values of 8.8 and 9.3, respectively, after preparation and the STPP solutions were adjusted to pH 9.3. The pH values corresponded to mean values of the 1020 steel and die-cast zinc used solutions in the corresponding detergents. These pH values were selected since 1020 carbon steel and die-cast zinc suffered the most corrosion and would, therefore, determine the pH conditions of soiled solutions.

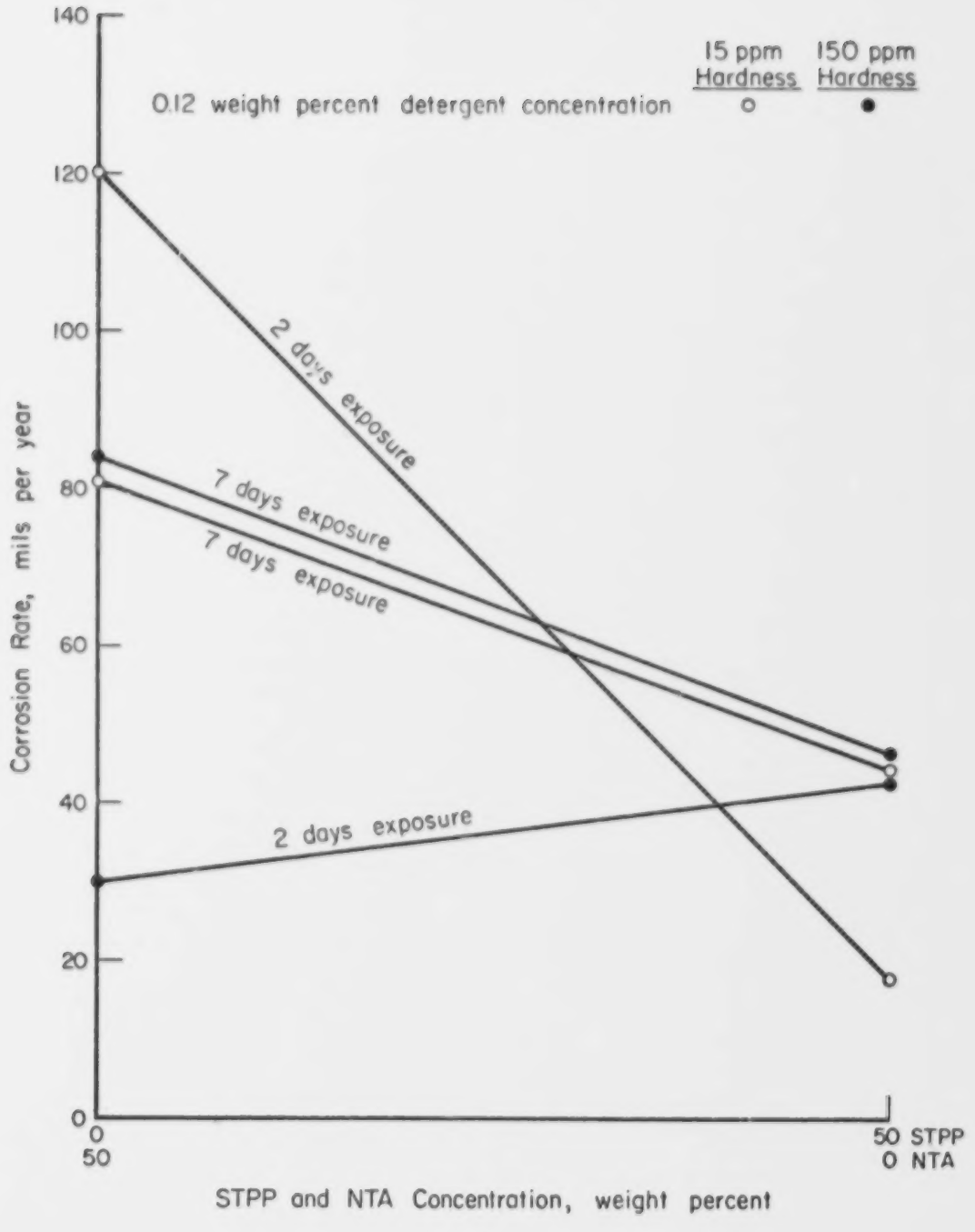


FIGURE 41. CORROSION RATE OF CAST IRON AS A FUNCTION OF STPP AND NTA CONCENTRATION AT 15 PPM AND 150 PPM WATER HARDNESS AND 130 F

Table 26. Summary of Data for Preparation of Soiled Detergent Solutions

Base Detergent Solution	Metal	Corrosion Rate, mdd	Metal Loss/Coupon In 2 Days, mg	Equivalent Weight of Metal Salt Added To 150 Ml Detergent Solution, mg
0.12 wt. percent of 50 wt. percent NTA and 15-ppm hardness	Fe	294[(a)]	117.3	537.2 $Fe_2(SO_4)_3$ $6H_2O$
	Cu	11.8	4.7	18.5 $CuSO_4$ $5H_2O$
	Zn	178	76.0	334.4 $ZnSO_4$ $7H_2O$
	Pb	125	52.9	77.2 $PbSO_4$
	Al	2.87	1.1	13.6 $Al_2(SO_4)_3$ $18H_2O$
0.12 wt percent of 50 wt. percent NTA and 150-ppm hardness	Fe	120[(a)]	47.8	218.9 $Fe_2(SO_4)_3$ $6H_2O$
	Cu	10.9	4.4	17.3 $CuSO_4$ $5H_2O$
	Zn	96.7	41.2	181.3 $ZnSO_4$ $7H_2O$
	Pb	105	44.4	64.8 $PbSO_4$
	Al	1.64	0.6	7.4 $Al_2(SO_4)_3$ $18H_2O$
0.12 wt. percent of 50 wt. percent STPP and 15-ppm hardness	Fe	40.8[(a)]	16.2	74.2 $Fe_2(SO_4)_3$ $6H_2O$
	Cu	6.0	2.4	9.4 $CuSO_4$ $5H_2O$
	Zn	104	44.4	195.4 $ZnSO_4$ $7H_2O$
	Pb	58.3	24.7	36.1 $PbSO_4$
	Al	2.65	1.0	12.3$Al_2(SO_4)_3$ $18H_2O$
0.12 wt. percent of 50 wt. percent STPP and 150-ppm hardness	Fe	124[(a)]	49.4	226.3 $Fe_2(SO_4)_3$ $6H_2O$
	Cu	3.0	1.2	4.7 $CuSO_4$ $5H_2O$
	Zn	56.5	24.2	106.5 $ZnSO_4$ $7H_2O$
	Pb	61.3	26.0	38.0 $PbSO_4$
	Al	1.62	0.6	7.4 $Al_2(SO_4)_3$ $18H_2O$

(a) 1020 Carbon steel.

The coupon-corrosion data for simulated soiled solutions are given in Table 24. Comparison of this weight-loss data to the 2-day weight-loss data in Table 23 for unsoiled solutions showed no consisten trends due to soiling. Thus, in NTA solutions in the soft-water condition, the corrosion rate decreased from 120 to 74 mils per year, but in hard water the corrosion rate increased from 29 to 37 mils per year with soiling. In STPP solutions and soft water the corrosion rate increased from 18 to 46 mils per year, but in hard waters the corrosion rate decreased from 45 to 12 mils per year with soiling. In the soiled solutions, it was evident, however, that the NTA solutions were more corrosive than the corresponding STPP solutions. In the soft-water solutions, the increased corrosivity factor was 1.6, and in hard-water solutions, 3.1. A greater increase in corrosivity of NTA solutions was observed in hard-water solutions, i.e., solutions of greater Cl^- content.

Corrosion products on coupons M17/M18 and M21/M22 from the NTA and STPP solutions, respectively, were found to contain principally δ-FeOOH. However, M17/M18 contained Fe_3O_4 and α-$NaFeO_2$ in small additions to the main phase of δ-FeOOH.

SECTION IX

DISCUSSION

Corrosion studies have been conducted on a variety of materials of construction associated with laundering: 1100 Aluminum, 260 Brass, electrolytic copper, die-cast zinc, Type 304 stainless steel, 201 Nickel, Type 420 stainless steel, chemical lead, and cast iron in a number of STPP- and NTA-based detergent solutions. The solutions were prepared as representative of heavy-duty granular detergents; i.e., 50-weight percent STPP or NTA at detergent concentrations of 0.06, 0.12, and 0.18 weight percent as likely to be employed by the average housewife in washing machines. The use of water of hardness values 15 and 150 ppm to relate to soft and hard water respectively, and solution temperatures of 130 and 160 F was also designed to represent conditions most likely to be met under laundering conditions. Coupon-weight-loss data were the main source of corrosion-rate information but was supplemented by limited electrochemical "linear polarization" studies.

It was readily apparent from the corrosion results that the materials investigated could be classed into four groups with regard to corrosion behavior in NTA and STPP-based detergents.

Group I included materials having very low corrosion rate in NTA and STPP solutions of the order of 0.01 to 0.15 mil per year. In this group were the materials in the following order of decreasing corrosion resistance: Type 304 stainless steel, 201 Nickel, and Type 420 stainless steel.

Group II included materials of moderate corrosion resistance with penetration of 0.2 to 3 mils per year. In this group were the materials: 260 Brass, electrolytic copper, and 1100 Aluminum which were quite similar with respect to their corrosion rates.

Group III included materials having poor corrosion resistance on the order of 2 to 60 mils per year. In this group were chemical lead, die-cast zinc, and 1020 carbon steel. Of these, chemical lead was slightly more corrosion resistant.

Group IV was represented by cast-iron soil pipe which had an extremely poor corrosion resistance material giving corrosion rates between 16 and 120 mils per year in the uncoated condition.

The materials within each of the above groups and the order of the groups with regard to corrosion behavior are as expected considering the usual corrosion behavior of the materials studied. Thus, it has been found that the usually very inert stainless steel and nickel materials are also the most corrosion resistant in the detergent solutions. On the other hand, the active base materials such as zinc alloys and carbon steel have been found to have poor corrosion resistance in the detergents. Copper, brass, and aluminum have shown the expected intermediate character for these materials.

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As might be predicted from electrochemical theory, the group classification of the materials with regard to corrosion rates was closely paralleled by the corrosion potentials of the various materials. Thus, Group I materials exhibited noble corrosion potentials of about -0.2 to -0.3 volt, Group III materials exhibited active corrosion potentials of about -0.6 to -0.9 volt, and Group II were of intermediate behavior with corrosion potentials of -0.2 to -0.4 volt.

In almost all experiments, it was found that the soft-water condition of 15-ppm hardness was more corrosive than the corresponding solution with hard water of 150-ppm hardness at a given detergent concentration. As discussed in Appendix B, the greater corrosivity of softer water is well established; the above results follow the usual trend. The greater corrosivity of the softer water was due to the greater concentration of builder component; i.e., STPP or NTA available from the detergent. In harder water, some of the STPP or NTA is used to soften the water by sequestering the magnesium and calcium ions and, therefore, is no longer available as a corrosion stimulator. Also, in softer water, the formation of protective magnesium and calcium scales is diminished.

In addition to the softer water being more corrosive for the investigated materials, it was also apparent that for any given water hardness, the corrosivity of the solutions increased with increase of detergent concentration from 0.06, 0.12 to 0.18 weight percent. This increase in corrosion rate was, in part, due to the increased availablility of sequestering compound for the corrosion process but probably also due to the associated increase of pH and decrease of specific resistance of the solutions as shown in Table 27. The increase of pH with increase of concentration was

Table 27. Specific Resistivity and pH Data for Detergent Solutions at Room Temperature

Detergent Concentration, weight percent	Hardness, ppm	50 Wt. Percent NTA Detergent		50 Wt. Percent STPP Detergent	
		pH	Specific Resistivity, ohm cm	pH	Specific Resistivity ohm cm
0.06	15	10.3	1800	10.0	1600
	150	9.9	1800	9.8	1500
0.12	15	10.6	1000	10.4	1000
	150	10.4	950	10.1	900
0.18	15	10.6	650	10.3	650
	150	10.6	700	10.2	600

probably due to the greater amount of OH^- formed through the hydrolysis of the STPP and NTA which are salts of weak acids and strong bases. It is apparent from Table 27 that NTA solutions were always slightly more alkaline by about 0.2 to 0.4 pH units than the corresponding STPP

solutions. This behavior was not due to a higher molar concentration of NTA at 50 weight percent builder since the molar ratio was 1.34 in favor of STPP, but was the result of the greater hydrolysis of the NTA detergent. The slightly smaller specific resistivities of the STPP solutions are probably associated with the larger ionic mobilities of the electrical species. The increased pH of the solutions would, of course, be less favorable to the amphoteric metals; e.g., aluminum, die-cast zinc, lead, and, tentatively, brass because of its zinc content, since these materials are strongly corroded in very alkaline solutions. Increased conductance favors corrosion processes by more readily allowing ionic transport in the solutions and the establishment of electrochemical cells on the surface of the materials. These data indicate that in either STPP- or NTA-based detergents, the use of higher-than-average detergent concentration (1 cup per 17-gallon washing machine) would favor increased corrosion. Lower-than-average detergent concentrations would be less corrosive. In all cases, however, soft make-up water could be more corrosive.

In addition to the soft water and increase of detergent concentration giving rise to higher corrosion rates, it was apparent that the NTA solutions in these conditions were almost always more corrosive than the corresponding STPP solutions. As discussed earlier, this behavior may be due, in part, to the higher pH values of these solutions. However, the most plausible explanation is that it is related to the greater sequestering power of NTA discussed in Appendix B. The increased corrosivity of the NTA solutions over STPP solutions was readily shown by the calculated increased corrosivity factors for the materials. These factors can be used to indicate how much more corrosive NTA detergent solutions are than corresponding STPP detergent solutions. These factors would thus also relate to the increased metal-ion pickup of the NTA detergent solutions or STPP detergent solutions as seen by a sewer treatment plant. The corrosivity factors are summarized in Table 28 for the least corrosion

Table 28. Summary of Increased Corrosivity Factors for NTA Solutions Over Corresponding STPP Solutions

Metal	Increased Corrosivity Factor
1100 Aluminum	1.0 to 1.3
260 Brass	1.3 to 5.0
Electrolytic Copper	1.5 to 3.8
Die-Cast Zinc	1.3 to 4.7
1020 Steel	1.0 to 7.1
Chemical Lead	1.0 to 3.1
Cast Iron	1.6 to 6.7

resistant metals of the construction materials employed in laundering. These factors were determined from weight-loss data for detergent solutions most likely to be employed by the housewife and at the average hot-water wash temperature of 130 F. The data clearly show the increased corrosivity of the NTA solutions. The increased corrosivity was particularly marked for cast iron and 1020 carbon steel and to a lesser extent for die-cast zinc

and 260 Brass. Electrolytic copper and chemical lead showed a smaller increase in corrosion rate and 1100 Aluminum was only very slightly effected. It is apparent, that for conditions corresponding to this work, the NTA detergent solutions could contain as much as 7 times more metal ions due to corrosion that would be brought about by similar STPP detergent solutions.

As shown in Table 28, cast-iron material, representative of uncoated cast-iron soil pipe, showed the greatest corrosivity factor. The high initial corrosion rates of 16 to 120 mils per year were reduced to 44 to 84 mils per year on longer exposure periods as graphitization occurred. It should be noted, of course, that the sewer pipe is supplied with a thin asphalt coating which affords some degree of protection for a short period. The corrosivity factors and corrosion rates, however, are applicable to the as-supplied pipe in undiluted detergent solutions. Corrosion of cast iron was still high at rates between 12 and 74 mils per year with simulated soiled detergent solutions thus indicating the inherent high corrosion susceptibility of this uncoated material.

It should be noted that the NTA and STPP detergent formulations used in these studies did not contain corrosion inhibitors as might normally be found in detergents. Thus, the formulations used here would probably be more corrosive than the corresponding commercial detergents. However, since neither the NTA nor the STPP detergent formulations used in the studies contained corrosion inhibitors, the relative corrosivity of the solutions should be significant and relate to the behavior of the corresponding commercial detergent formulations

With the exception of die-cast zinc and 1020 carbon steel, the corrosion behavior of the investigated materials was usually in the form of general even corrosion for both STPP and NTA solutions. However, die-cast zinc exhibited pitting corrosion in many experiments. The pitting was usually more severe in the solutions representative of the average detergent strength used by the housewife (i.e., 0.12 weight percent detergent). Furthermore, the pitting corrosion extended as fine corrosion paths below the pits. It is doubtful that the pitting rates of 180 to 540 mils per year measured over 2 days' exposure would be sustained at this rate, but the inherent susceptibility of this material is indicated. 1020 steel exhibited localized attack in STPP and NTA solutions representative of average and greater than average detergent concentrations (i.e., 0.12 and 0.18 weight percent). This corrosion, however, was usually not deep and the associated etched appearance did not penetrate into the material intergranularly as the surface appearance suggested. Although 260 Brass corroded in many STPP solutions, it was apparent that some dezincification occurred. The dezincification was confined to the surface and did not penetrate into the material. The dezincification may be associated with a limited solution pH range of about 9.9 to 10.4.

Linear polarization measurements to evaluate corrosion rates did not correlate well with weight-loss data with the exception of results for 1020 carbon steel and probably Type 304 and 420 stainless steel and 201 Nickel. Because of good overall precision of the weight-loss data using duplicate samples, it was concluded that weight-loss data were the most significant. The poor correlation with weight-loss data in terms of measured corrosion rates was probably due to the formation of poorly conducting films on the materials. The films gave a low assessment of corrosion rate in this method which effectively depends on measuring the electrical

resistance of the corrosion process. Using the results of this method to compare behavior within a given system, it appeared that the use of mixed 37.5 STPP-1.25 NTA-based detergents did not significantly change corrosion behavior over that noted for the pure 50 STPP- or 50 SNTA-based detergents.

Since the joint statement (Appendix A) on December 18, 1970, by the Environmental Protection Agency Administrator and the Surgeon General, concerning the voluntary removal of NTA from detergents, a variety of phosphate and NTA "free" detergents have appeared on the market. These products appear to be based upon soda ash, silicates, borax, or polyelectrolytes or mixtures of these with other minor ingredients.[6] The corrosivity of such detergent formulations to materials used in laundering and sewer systems was not determined from a scan of the open literature, and thus some concern must be expressed for their use.

SECTION X

ACKNOWLEDGMENTS

This work was performed under EPA, WQO Contract No. 14-12-943. Liaison was maintained with Mr. Charles E. Myers, Project Officer, of the Division of Process Research and Development, WQO, EPA. The support of the project by the WQO, EPA, under the guidance of Mr. Charles E. Myers, is acknowledged and appreciated.

The provision of the basic ingredients for preparation of the heavy-duty granular detergents and useful advice by The Procter & Gamble Company, Cincinnati, Ohio, is appreciated.

SECTION XI

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SECTION XII

GLOSSARY

Builder - A substance added to or used with detergents to increase their cleaning action.

Descaling - The removal of corrosion products from a corroded specimen, with a minimum removal of base metal so that underlying base metal can be examined and/or metal weight loss can be determined.

Detergent - Any of numerous synthetic water-soluble or liquid-organic preparations that are chemically different from soaps but resemble them in the ability to emulsify oils and hold dirt in suspension.

Dezincification - Corrosion of a zinc containing alloy, usually brass, involving loss of zinc and a residue or deposit in-situ of one or more less active constituents, usually copper.

General Corrosion - Corrosion producing uniform penetration of a surface.

Graphitization - Corrosion of gray cast iron in which the metallic constituents are converted to corrosion products leaving the graphite intact.

Linear Polarization - A method in which small potential changes ΔE of the order of 10mV applied to an electrode and the resultant current flow ΔI are related through the linear relationship $\Delta E = R\Delta I$ where R is a constant. R, termed the "polarization resistance", is related to the corrosion rate of the electrode material. Thus, the linear polarization method enables corrosion rates to be determined.

Localized Corrosion - Corrosion producing nonuniform penetration of a surface which ranges from small areas of general corrosion to intense attack at one or small areas.

pH - A measure of the hydrogen-ion concentration of a sample which represents the logarithm of the reciprocal (negative logarithm) of the activity of hydrogen ions calculated as follows:

$$pH = \log 1/(H^+) = - \log (H^+),$$

where H^+ = activity of hydrogen ions.

Pitting Corrosion - An extreme form of localized corrosion giving rise to cavities or pits in the surface which have a small width-to-depth ratio (approximately less than 6:1).

Potentiodynamic - The technique of varying the potential of an electrode in a continuous manner at a preset rate. It is frequently employed to prepare polarization plots.

Sequestration - The formation of a soluble complex chemical from the reaction of a simple metal ion with a complexing chemical species.

Specific Resistivity - The resistance in ohms measured between two electrodes which cover opposite faces of a centimeter cube in aqueous solution at a specific temperature.

Tafel Slope - Application of large potentials to an electrode frequently yields a current-potential relationship over a region which can be approximated by

$$E = a + b\ln/I/,$$

where E is the electrode potential
I is the observed current density
a and b are constants.

The constant b is known as the Tafel slope.

SECTION XIII

APPENDIX

A. STATEMENT ON NTA, DECEMBER 18, 1970

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A. STATEMENT ON NTA, DECEMBER 18, 1970

Environmental Protection Agency Administrator, William D. Ruckelshaus, and Surgeon General, Jesse L. Steinfeld, said today in a joint statement:

> "We commend the major detergent manufacturers for their voluntary action to discontinue use of NTA (nitrilotriacetic acid) in the manufacturing of detergents, pending further tests and review of recently completed animal studies, in order to protect the Nation's health from any potential hazard. NTA, a chemical being substituted for phosphates in some detergents, has been used in gradually increasing quantities to reduce the possible contribution of detergent phosphates to accelerated aging of surface waters in the environment. The aging process, known technically as eutrophication, results from excessive growth of aquatic plant life; overgrowth of algae and nuisance aquatic weeds has a deleterious effect on aquatic life and can have severe impact on water quality. Although the industry was urged to make the substitution of NTA for phosphates, and NTA was subjected to extensive testing, recently completed studies of the biological activity of NTA combined with heavy metals have raised concern that the projected uses of NTA may constitute a hazard to health."

BACKGROUND

Early studies, both those conducted by the Federal Water Quality Administration (FWQA) and the industry, concentrated on the more conventional kinds of toxicology studies using NTA alone. The studies which provide the basis for today's action were initiated in the National Institute of Environmental Health Sciences of the National Institutes of Health of the Department of Health, Education, and Welfare last spring at the request of the FWQA, formerly of the Department of the Interior and now an agency of the Environmental Protection Agency. The NIEHS was asked to examine the possibility of adverse reactions (birth abnormalities) secondary to exposure to NTA itself or to NTA administered simultaneously with heavy metals. At the dosages employed in the NIEHS studies, which were considerably higher than would ordinarily be encountered by the human population, the administration of two heavy metals (cadmium and methyl mercury) simultaneously with NTA to two species of animals (rats and mice) yielded a significant increase in embryo toxicity and congenital abnormalities in the animals studied over the results with the same dosage of the metals alone.

NTA alters the toxicity of metals by affecting their entry, distribution, and concentration in the tissues. Of particular concern is the increased rate of transmission of metals across the placenta to the fetus which accounts for the fetal toxicity and congenital abnormalities produced in animals in the NIEHS studies. This potentiating effect of NTA with metals, together with the projected scale of use of NTA from today's beginning 100-200 million pounds per year to as much as a billion or more pounds per year over the next few years, was the basis for today's action.

There is no evidence at this time to indicate that anyone has been or is being harmed by the combination of NTA with metals in the environment. However, prudence dictates not permitting a situation to develop in which harm may occur to man from the effects of the projected uses of NTA.

RECOMMENDATIONS

Representatives of the major detergent manufacturers, though they have not had an opportunity to analyze fully the NIEHS data, nevertheless have agreed to discontinue use of NTA in the manufacture of soap and detergent products, pending further tests and review of these and other studies. Existing supplies of NTA-detergent products may be depleted through normal distribution. We want to reemphasize that we have no evidence to indicate that anyone has been harmed or is being harmed by these products.

However, there are certain areas where prudence would dictate that these products should not be used. We recommend that NTA-detergent products not be used in certain limited areas which have both well water supplies and septic tanks, and in which these treatment systems are operating under completely anaerobic conditions and where short-circuiting of septic tank effluent directly into well supplies is occurring. The products are: Amway SA-8, Cheer, Gain, H.L.D., K-50, Laundri-Maid, Liquid All, Loft, Phos-Free, Roundy's, Sav-us, Ultra, and Valley-Dew. (This list is not complete).

In responding to one environmental problem, great care must be exercised to assure that the alternative does not pose equal or greater hazards to the environment or to human health. This is certainly the case with detergents in view of the massive quantities produced and ubiquitous nature of their distribution. It should be recognized that regulatory efforts by Federal, State, and local officials must be conducted intelligently with full awareness of potential secondary effects of those efforts.

As important as the prompt reduction of phosphates in detergents is in reducing the load of algae nutrients in water, we must reluctantly conclude that NTA does not appear to be an appropriate alternative at this time. We continue to urge that phosphates and other nutrients be removed from waste waters by the application of proper waste treatment methods across the country. Additional studies of NTA are now underway, both by the industry and within the Government. Intensive study of other phosphate substitutes will be necessary to assure, to the extent possible, that they do not present a similar predicament.

B. CORROSION EFFECTS OF NTA WITH SPECIAL REFERENCE TO ITS USE AS A BUILDER TO REPLACE POLYPHOSPHATES IN DETERGENT FORMULATIONS

INTRODUCTION

Nitrilotriacetic acid (NTA) originated in Germany during the 30's and was first marketed under the name "Trilon A".[1] Its use as a sequestering agent, particularly in detergent formulations, was not economic until recently. During the 60's, more economical methods of manufacture were developed resulting in both a reduction in cost and greater availability.[2,3] In recent years, the use of NTA as a detergent builder has expanded rapidly. As a detergent builder, best results are obtained when it is used to replace part but not all of the polyphosphate in the detergent mix.[4] However, it appears more difficult to process NTA into detergent formulations.[5]

CHEMISTRY OF AMINO POLYCARBOXYLIC ACIDS

Of the amino polycarboxylic acids, EDTA (ethylene diamine tetracetic acid) is the best known and most widely used.[1,6-8] The related product NTA (nitrilotriacetic acid) has only recently become widely known.[2] The chemical structure of the trisodium salt of NTA is shown in Figure 1.[9]

NTA has a capability similar to EDTA to sequester metal ions. Details of the chelating chemistry of NTA is rather limited; however, one can obtain an approximate idea of its chemical performance by studying the behavior of EDTA.

The sodium salts of EDTA and NTA are highly soluble. For the trisodium salt of NTA, saturation in water is reached at about 40 percent by weight.[1] Similarly the solubility of the tetrasodium salt of EDTA is about 51 percent by weight.[10] As might be expected, each of these sodium salts, which is the salt of a weak acid, has a strong alkaline reaction.

EDTA will sequester almost every polyvalent metal in the periodic table. Usually the molecular ratio of the metal ion chelated to EDTA is one to one.[7] Similarly NTA will complex or chelate most polyvalent cations.[2] The metal is bound into the chelate structure by both ionic and covalent bonds forming an extremely stable complex. This effectively deactivates the metal and eliminates the detrimental effects often caused by metal ions in aqueous systems.

The sequestering activity is affected by the pH since there is competition between hydrogen ions and metal ions. At high pH, say 10 and above, the complexing of metal ions is most effective.

In hard waters, NTA (or EDTA) will, in effect, soften the water by the removal of calcium and magnesium ions from solution. This action prevents the formation of insoluble soaps and precipitates. The alkaline earth complexes are highly stable. The reaction of NTA and EDTA in sequestering calcium is shown in Figure 2.[2] On a weight basis, NTA will chelate almost 50 percent more calcium ions than will EDTA. However, the stability constant for any given NTA-sequestered cation is invariably lower than that for the same EDTA-sequestered cation. This may require an excess above the stoichiometric amount of NTA to insure completion of the sequestering action in some applications.[2]

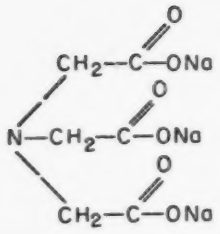

FIGURE 1. STRUCTURE OF THE TRISODIUM SALT OF NTA (TRISODIUM NITRILO TRIACETATE (9)

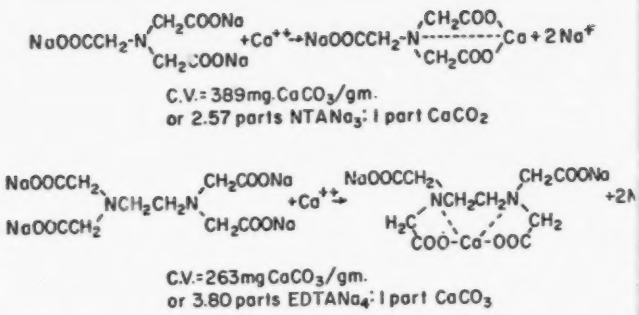

FIGURE 2. CHELATING CAPACITY OF THE SODIUM SALT OF NTA COMPARED WITH THE SODIUM SALT OF EDTA (2)

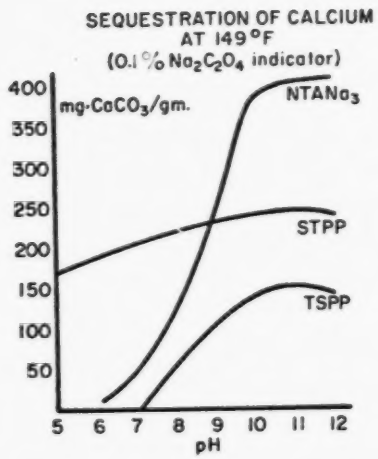

FIGURE 3. A COMPARISON OF THE SEQUESTRATION OF CALCIUM BY NTA AND BY POLYPHOSPHATES AT DIFFERENT pH LEVELS (2)

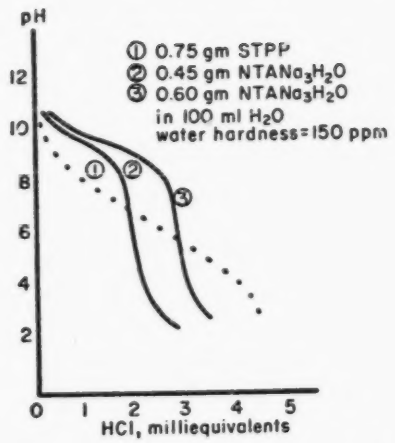

FIGURE 4. BUFFER CAPACITY OF NTA VERSUS TRISODIUM POLYPHOSPHATE (STPP) (2)

Polyphosphates, as well as NTA, are more effective in sequestering calcium at the higher pH levels. At 140 F and at a pH of 10 and above, it can be seen from Figure 3 that the trisodium salt of NTA is roughly twice as effective as STPP and three times as effective as the tetrasodium pyrophosphate (TSPP) in sequestering calcium.[2] Of concern in its effect on the corrosion environment is NTA's buffering capacity. As can be seen in Figure 4, it requires more acid to lower the pH from say 11 to 8, with NTA in solution than is the case with STPP.[2] Thus the sequestering capability of NTA in alkaline solution is less readily disturbed.

In the typical detergent formula, NTA can be used to replace part or all of the polyphosphate. NTA achieves a higher brightness level on fabrics than does STPP at about one-half the quantity of builder.[2] Other benefits of NTA as a builder in detergent formulation include (a) lower mineralization of cotton fabric washed in hard water compared to results when using STPP as a builder, (b) good foam stabilization, (c) improved rinsability of detergent components from fabrics and hard surfaces because of the greater solubility of NTA versus STPP, (d) stabilization of minor ingredients such as bleaches, brightners, and sanitizing agents.[2,3,5]

The important differences between the amino acid chelating agents; e.g., NTA and the polyphosphates, are:[3,11]

(1) The amino acids can combine with a wider range of polyvalent metal ions than the polyphosphates.

(2) The polyphosphates tend to revert to the simple phosphate form as the result of excessive acid or alkaline conditions. High temperatures also increase this tendency. For detergents normally packaged in powdered form, this instability is usually not a factor but for concentrated liquid detergents, formulators often elect to omit the polyphosphate because of stability problems.

(3) Polyphosphates exhibit a so-called threshold effect, a characteristic not present in amino acid compounds. A few parts per million of polyphosphate will keep much larger molar quantities of chemical compounds, which would otherwise tend to precipitate, in solution.

Because the effects of NTA and STPP, as builders, are not identical, the most effective detergent formulations incorporate a combination of both products.[2,3] A molar ratio of sodium tripolyphosphate to sodium nitrilotriacetate of 3:1 to 1:3 is found to give good results.[4]

CORROSION REACTIONS OF NTA AND POLYPHOSPHATES

Polyphosphates have been used in water systems for scale control and for inhibition of steel corrosion. Protection appears to be the result of the deposition of a film at the cathodic sites.[12]

Under the alkaline conditions and concentrations used in detergent solutions, polyphosphates are found to be corrosive to alloys of aluminum, zinc, and to copper-nickel-zinc alloys (German silvers).[4] When NTA is substituted for polyphosphate, the same metals are affected.[4]

Factors Affecting Corrosivity

NTA solutions can be expected to be corrosive to metals because of the following factors:

(1) NTA ties up the alkali-metal ions, particularly calcium, into soluble complexes. This prevents the formation of protective scales, such as calcium carbonate, in effect, allows corrosion to proceed.

(2) As metal ions from corrosion reactions enter solution they are sequestered by the NTA. This prevents the formation of protective films of corrosion products. Existing films may be sequestered by the NTA and thus removed. In addition, the low concentration of unsequestered metal ions in solution stimulates the corrosion reaction by preventing the attainment of equilibrium.

(3) NTA penetrates a variety of protective films formed by corrosion inhibitors.[4]

Many of these reactions are similar to those of the polyphosphates. Phosphates complex calcium ions (Item 1 above) and also sequester metal ions from corrosion reactions (Item 2).[13] On the other hand, the presence of low levels of polyphosphate, unlike NTA, will often increase the effectiveness of an inhibitor.

Use of Inhibitors

One problem with high levels of polyphosphates in detergent solutions has been the tendency toward corrosion of the "white metals". The necessity for the inhibition of phosphate-bearing detergents is well established.[4] For example, aluminum corrosion can be inhibited by adding silicates.[4,14] Without the silicates, the polyphosphates will maintain a fresh surface for initial attack. The proper silicate, if added, will be chemisorbed on the metal and prevent further sequestration. It is found that aluminum corrosion is effectively inhibited by sodium silicate having a ratio of SiO_2 : Na_2O of about 1.6.[4,14] The inhibition of corrosion of copper-nickel-zinc alloys in phosphate containing detergents can be accomplished by benzotriazole.[4]

Neither of the above inhibitors is effective toward zinc or "Zamak"[3] with either polyphosphate or NTA as builders. The corrosion rate can be inhibited to an acceptable range by the addition of an alkyl phosphonate according to a British patent.[4]

Table 1. Corrosion of Zamak 3[a] by Detergent[b] Containing Sodium Nitrilotriacetate (NTA) With and Without Inhibitor[c] After 6 Hours in Agitated Solutions at 140 F.[4]

Detergent Concentration	Type of Water	Loss in Mg/Sq Dm/Day	
		Inhibited	Uninhibited
0.2%	Hard[d]	39	355
0.5%	Distilled	238	688

(a) Nominal composition, 4 Al, 0.04 Mg, remainder Zn.
(b) See Table 2, for composition.
(c) Inhibitor is "0.3 percent of random octadecyl phosphonic acid prepared by adding phosphorous acid to a random mixture of octadecenes using gamma radiation as a source of radicals".
(d) Hardness = 8.4 grains per imperial gallon or 120 ppm.

See Table 1 for composition of Zamak.

Examples of Corrosion Behavior

The composition of a detergent containing NTA is given in Table 2.

Table 2. Composition of a Spray-Dried Granular Detergent Containing NTA in Percent by Weight[4]

	Percent
Sodium straight chain alkyl benzene sulphonate having an average chain length of 13 carbon atoms	13.3
Sodium tripolyphosphate (STPP)	41.4
Sodium nitrilotriacetate (NTA)	9.6
Sodium silicate having a SiO_2 : Na_2O weight ration of 1.6	10.0
Marine oil fatty acids	0.5
Tallow fatty acids	1.5
Sodium carboxymethylcellulose	0.33
Sodium sulfate	11.26
Water	11.00
Miscellaneous ingredients including perfume, optical brighteners, and pigments	1.11

Note that the ratio of STPP to NTA is about 4:1. The corrosion rates given in Table 1 are for Zamak 3 in agitated detergent solutions at 140 F for 6 hours. The hard water (equivalent to 120 parts per million by weight)

contained a 0.2 percent concentration of detergent by weight. The "random octadecyl phosphonic acid" inhibitor, at 0.3 percent strength, reduced the corrosion rate to about 1/9 of that of the uninhibited solution. The inhibition in the distilled water solution with 0.5 percent detergent was only partially effective.

In another experiment, aluminum and Zamak 3 were found to be corroded by 0.35 percent detergent solutions, using the same two waters as in the Zamak 3 tests above. The detergent composition was:

Sodium tetrapropylene benzene sulfonate	20%
Sodium tripolyphosphate	50%
Sodium sulfate	25%
Inhibitor	5%

In this experiment, the exposure was for 3 hours at 140 F at a pH of 9.5. Adding 5 percent phosphonic corrosion inhibitor, e.g., 10 nonadecyl phosphonic acid or pentadecyl benzyl phosphonic acid resulted in inhibition not only for aluminum but also for Zamak 3.

When NTA is substituted for the polyphosphate, the corrosion rates also are unacceptable. However, the attack on both metals is effectively inhibited by phosphonic corrosion inhibitors.

DISCUSSION

Much of the literature on NTA discusses analytical techniques, problems of sewerage treatment, efficiency as a detergent builder, and packaging problems. Corrosion data are almost nonexistent in the open literature.

One gathers from a study of detergents in general that there is an almost endless variety on the market. Many of these detergent formulations tend to be corrosive, and manufacturers of laundry and washing machines have found it necessary to construct their units of corrosion-resistant materials.[4,14-17] The introduction of NTA for part of the polyphosphate does not appear to have altered the situation as far as domestic washing machines are concerned. A recent suggestion is to replace part of the polyphosphate builder[5] by increasing the amount of surface-active agent to partially compensate for the change. It is not easy to predict how these alterations in formulation will reflect the corrosivity of detergent solutions to white metals such as zinc and aluminum. Builders such as sodium carbonate may be required to maintain alkalinity.

No indication was found in the literature that NTA-bearing, spent-detergent solutions are more corrosive to sewer lines and to sewerage plants than is the case for phosphate-based detergents.

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(1) Accession Number | (2) Field & Group | Subject | SELECTED WATER RESOURCES ABSTRACTS Input Transaction Form

(5) Organization

Battelle Memorial Institute, Columbus Laboratories

(6) Title

Corrosion Potential of NTA in Detergent Formulations

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(16) Project Designation

EPA, WQO Contract No. 14-12-943

(21) Note

(22) Citation

(23) Descriptors (Starred First) - corrosion, eutrophication, detergents, pollution, phosphates, plumbing, metals, stainless steels

(25) Identifiers (Starred First)
NTA, STPP, laundering equipment, polarization studies

(27) Abstract

Laboratory studies were conducted to determine the corrosion potential of nitrilotriacetic acid (NTA) as a substitute for sodium tripolyphosphate (STPP) in detergents. Coupon-weight loss and linear polarization studies were employed to investigate the corrosion of typical materials of construction which might be subject to exposure to NTA in normal use in laundering.

Detergent formulations were used which were representative of heavy-duty granular detergents. Solutions of 0.06, 0.12, and 0.18 weight percent using 15- and 150-ppm water hardness and temperatures of 130 and 160 F represented laundering conditions used by the average housewife

NTA-based detergents were more corrosive by a factor between 1 and 7 to the materials 1100 Aluminum, 260 Brass, electrolytic copper, die-cast zinc, 1020 carbon steel and chemical lead. Corrosion was generally greatest in NTA and STPP solutions with soft water. In both soft and hard waters, corrosivity increased with increase of detergent concentration.

Types 304 and 420 stainless steel and 201 Nickel were very corrosion resistant (0.01 to 0.15 mil per year), 260 Brass, electrolytic copper and 1100 Aluminum were moderately resistant (0.2 to 3 mils per year) and die-cast zinc, 1020 carbon steel and chemical lead poorly corrosion resistant at rates of 2 to 60 mils per year. Cast iron showed extreme corrosion in NTA solutions with corrosion rates between 30 and 120 mils per year. NTA detergents could increase metal ion pickup at a sewage plant by a factor between 1 and 7.

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